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# K-Absorption Edges of Ni, Cu, Zn and their Compounds

By

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**Abstract**

Investigating the K-absorption limits and their structures for the elements Ni, Cu, Zn and their compounds, we found the following facts: that the appearance of the structure of the absorption edge for a pure element was very different from that for its compounds and that the structures of the absorption edges seemed to depend upon the crystal forms of the substances.

## Experimental Method

The photograms were taken by the absorption screen method with a spectrograph of Seeman's "Loch Kamera" type made in this laboratory. The absorption screens for the pure elements were prepared by rolling the metals, and the absorption screens for the compounds by rubbing them in the form of a fine powder on filter paper and dropping Zapon Enamel on them. Calcite was used as the analyser throughout our experiments. As the source of X-rays, a Shearer metal tube which was evacuated by a Cenco oil pump was used. The tube was excited by a transformer at about 60 kilovolts and the current through it was about 9 milli-amperes.

## Results

(1) The main edge.

To calculate the wave-length difference between the main absorption limits of the pure metal and its compounds, several photograms were taken for each sample. The mean values of the edges are shown in Table 1. We also compared the separation between the main

edge of a pure metal and its oxide by taking the two photograms on one plate as shown in Plate Group A. The results are summarized in Table 2. For the main edge, we read the shorter wave-length limit

Table 1.

The wave-lengths of the K-absorption main edges obtained by taking the mean of a few plates.

(A) Ni and its compounds.

| Substance | Valency | λ(x. u) of the main edge | $\nu/R$ | $\Delta\lambda$ | $\Delta(\nu/R)$ | $\Delta V$ |
|---|---|---|---|---|---|---|
| Ni | 0 | 1482.71 | 614.60 | 0 | 0 | 0 |
| NiO | 2 | 1482.68 | 614.61 | 0.03 | 0.01 | 0.14 |
| $Ni(SO_4)_2$ | 4 | 1482.40 | 614.72 | 0.31 | 0.12 | 1.63 |

(B) Cu and its compounds.

| | | | | | | |
|---|---|---|---|---|---|---|
| Cu | 0 | 1375.77 | 662.37 | 0 | 0 | 0 |
| $Cu_2O$ | 1 | 1375.73 | 662.39 | 0.04 | 0.02 | 0.27 |
| CuO | 2 | 1375.32 | 662.58 | 0.45 | 0.21 | 2.84 |

(C) Zn and its Compounds.

| | | | | | | |
|---|---|---|---|---|---|---|
| Zn | 0 | 1279.52 | 712.19 | 0 | 0 | 0 |
| ZnS (Wurtzite) | 2 | 1279.02 | 712.48 | 0.50 | 0.29 | 3.39 |
| ZnS (Zinc Blende) | 2 | 1279.27 | 712.34 | 0.25 | 0.15 | 2.03 |
| ZnO | 2 | 1279.34 | 712.30 | 0.18 | 0.11 | 1.49 |

Table 2.

The wave-lengths of the K-absorption main edge obtained from two photograms on one plate.

(A)

| Substance | Valency | λ(x. u) of the main edge | $\nu/R$ | $\Delta\lambda$ | $\Delta\nu/R$ | $\Delta V$ | Ref. lines |
|---|---|---|---|---|---|---|---|
| Ni | 0 | 1482.81 | 614.56 | 0 | 0 | 0 | Cu K $\alpha_1$ |
| NiO | 2 | 1482.24 | 614.79 | 0.57 | 0.23 | 3.11 | Cu K $\beta_1$ |

(B)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cu | 0 | 1376.01 | 662.26 | 0 | 0 | 0 | Cu K $\alpha_1$ |
| $Cu_2O$ | 1 | 1375.71 | 662.40 | 0.30 | 0.14 | 0.90 | Cu K $\beta_1$ |

(C)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cu | 0 | 1375.69 | 662.41 | 0 | 0 | 0 | Zn K $\alpha_1$ |
| CuO | 2 | 1374.94 | 662.77 | 0.75 | 0.36 | 4.88 | Cu K $\beta_1$ |

(D)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Zn | 0 | 1279.97 | 711.95 | 0 | 0 | 0 | Zn K $\alpha_1$ |
| ZnO | 2 | 1279.67 | 712.11 | 0.30 | 0.16 | 2.17 | Zn K $\beta_1$ |

of the blackening by a comparator. The wave-lengths of the reference lines were taken from Siegbahn's "The spectroscopy of X-rays". The dispersions on our plates are about 15 x. u. per mm. Lindh[1] has already reported that the wave-lengths of the K-edge of an element in the state of compounds are a few x. u. shorter than in the case of the pure element and that the difference increases with the valencies of its compounds. From our results we can also see the tendency to shift to the shorter wave-length side in accordance with the valency for an element in the state of compounds. Our result for CuO is a little smaller than that obtained by Owen and Williams.[2]

(2) The structure of the edge.

The structure of the edge which appeared on the shorter wave-length side of the main edge, has been investigated by G. A. Lindsay,[3] R. de L. Kronig,[4] D. Coster,[5] J. D. Hanawalt,[6] and A. E. Lindh,[7] etc. The former two discussed the problem of the origin of this structure. Lindsay explained the fine structure by considering that in one absorption act not only one electron from the K orbit but many electrons transit to the outer orbits simultaneously, and corresponding to the

1. Axel E. Lindh: ZS. f. Phys. **63**, 106. (1930).
   Hand. d. Experimental Physik: 24, (2) Röntgenspektroskopie, Kap. 10, S. 281.
2. Owen and Williams: Pro. Roy. Soc. London. (A) **123**, 282. (1931).
3. G. A. Lindsay and G. Van Dyke: Phys. Rev. **28**, 613. (1926).
   G. A. Lindsay and H. R. Voorhees: Phil. Mag. **6**, 910. (1928).
   Ben Kievit and G. A. Lindsay: Phys. Rev. **36**, 648. (1930).
   G. A. Lindsay: ZS. f. Phys. **71**, 735. (1931).
4. R. de L. Kronig: ZS. f. Phys. **70**, 317. (1931).
5. D. Coster and J. H. van der Tuuk: ZS. f. Phys, **37**, 367. (1926).
   D. Coster and M. Wolf: Nature, **124**, 652. (1929).
   D. Coster and J. Veldkamp: ZS. f. Phys. **70**, 306. (1931).
6. J. D. Hanawalt: Phys. Rev. **37**, 715. (1931).
   J. D. Hanawalt: ZS. f. Phys. **70**, 293. (1931).
7. Axel E. Lindh: loc. cit. (the former)

Table 3

The Wave-length Difference ($\Delta\lambda$) and the Energy Difference ($\Delta(\nu/R.)\ \Delta V$) of the Fine Structure from the K-Absorption edge.

| | | a | a′ | b | b′ | c | c′ | d | d′ |
|---|---|---|---|---|---|---|---|---|---|
| Ni | $\Delta\lambda$ | 2.78 | 6.06 | 7.71 | 14.27 | 17.56 | 24.12 | 29.87 | 34.80 |
| | $\Delta(\nu/R)$ | 1.15 | 2.52 | 3.21 | 5.97 | 7.37 | 10.16 | 12.63 | 14.77 |
| | $\Delta V$ | 15.58 | 34.14 | 43.49 | 80.88 | 99.84 | 137.64 | 171.10 | 200.09 |
| NiO | $\Delta\lambda$ | 2.81 | 5.29 | 6.12 | 9.43 | 10.25 | 16.87 | 22.67 | 24.32 |
| | $\Delta(\nu/R)$ | 1.17 | 2.21 | 2.56 | 3.94 | 4.29 | 7.08 | 9.54 | 10.25 |
| | $\Delta V$ | 15.85 | 29.94 | 34.68 | 53.38 | 58.12 | 95.91 | 129.24 | 138.86 |
| $Ni(So_4)_2$ | $\Delta\lambda$ | 2.48 | 7.71 | 12.93 | 18.16 | 29.92 | 36.46 | | |
| | $\Delta(\nu/R)$ | 1.03 | 3.22 | 5.42 | 7.63 | 12.67 | 15.51 | | |
| | $\Delta V$ | 13.95 | 43.62 | 73.42 | 103.36 | 171.64 | 210.11 | | |
| Cu | $\Delta\lambda$ | 1.48 | 4.79 | 5.62 | 10.57 | 13.05 | 19.67 | 22.15 | 27.10 |
| | $\Delta(\nu/R)$ | 0.71 | 2.31 | 2.72 | 5.13 | 6.34 | 9.61 | 10.84 | 13.31 |
| | $\Delta V$ | 9.62 | 31.29 | 36.85 | 69.50 | 85.89 | 130.19 | 146.85 | 180.31 |
| $Cu_2O$ | $\Delta\lambda$ | 1.82 | 8.46 | 13.45 | 18.43 | 25.07 | 31.72 | | |
| | $\Delta(\nu/R)$ | 0.88 | 4.09 | 6.54 | 8.99 | 12.29 | 15.63 | | |
| | $\Delta V$ | 11.92 | 55.41 | 88.60 | 121.79 | 166.49 | 211.74 | | |
| CuO | $\Delta\lambda$ | 2.33 | 3.67 | 4.33 | 7.66 | 10.16 | 13.50 | 15.99 | 20.99 |
| | $\Delta(\nu/R)$ | 1.12 | 1.77 | 2.09 | 3.71 | 4.93 | 6.56 | 7.79 | 10.26 |
| | $\Delta V$ | 15.17 | 23.98 | 28.31 | 50.26 | 66.79 | 88.87 | 105.53 | 138.99 |
| Zn | $\Delta\lambda$ | 1.37 | 3.62 | 5.13 | 8.13 | 9.64 | 14.15 | 17.16 | 21.67 |
| | $\Delta(\nu/R)$ | 0.76 | 2.02 | 2.87 | 4.56 | 5.41 | 7.97 | 9.70 | 12.28 |
| | $\Delta V$ | 10.30 | 27.36 | 38.88 | 61.77 | 73.29 | 107.97 | 131.41 | 166.36 |
| ZnO | $\Delta\lambda$ | 1.64 | 5.98 | 10.48 | 14.22 | 17.97 | 26.96 | 31.45 | 40.44 |
| | $\Delta(\nu/R)$ | 0.91 | 3.35 | 5.88 | 8.00 | 10.14 | 15.33 | 17.94 | 23.24 |
| | $\Delta V$ | 12.33 | 45.38 | 79.66 | 108.38 | 137.37 | 207.68 | 243.03 | 314.83 |
| ZnS Zinc Blende | $\Delta\lambda$ | 1.21 | 7.05 | 8.51 | 14.35 | 15.81 | 21.65 | 28.95 | 34.79 |
| | $\Delta(\nu/R)$ | 0.67 | 3.95 | 4.77 | 8.07 | 8.91 | 12.26 | 16.49 | 19.91 |
| | $\Delta V$ | 9.08 | 53.51 | 64.62 | 109.32 | 120.70 | 166.09 | 223.39 | 269.72 |
| ZnS Wurtzite | $\Delta\lambda$ | 1.05 | 5.51 | 6.99 | 14.42 | 16.64 | 24.07 | 30.01 | 35.95 |
| | $\Delta(\nu/R)$ | 0.58 | 3.09 | 3.91 | 8.12 | 9.38 | 13.66 | 17.11 | 20.60 |
| | $\Delta V$ | 7.86 | 41.86 | 52.97 | 110.00 | 127.07 | 185.05 | 231.79 | 279.07 |

| e | e′ | f | f′ | g | g′ | h | h′ | i | i′ |
|---|---|---|---|---|---|---|---|---|---|
| 37.26 | 38.90 | 43.83 | 53.68 | 60.25 | 71.74 | | | | |
| 15.84 | 16.56 | 18.72 | 23.08 | 26.04 | 31.24 | | | | |
| 214.58 | 224.34 | 253.60 | 312.66 | 352.76 | 423.21 | | | | |
| 30.94 | 35.91 | 46.66 | 48.32 | 50.80 | 52.46 | 58.25 | 64.87 | 68.18 | 81.42 |
| 13.10 | 15.25 | 19.97 | 20.70 | 21.80 | 22.54 | 25.13 | 28.11 | 29.61 | 35.70 |
| 177.47 | 206.59 | 270.53 | 280.42 | 295.32 | 305.35 | 340.44 | 380.81 | 401.13 | 483.63 |
| | | | | | | | | | |
| 29.58 | 31.24 | 35.37 | 41.98 | 46.94 | 56.86 | | | | |
| 14.56 | 15.40 | 17.49 | 20.86 | 23.41 | 28.57 | | | | |
| 197.24 | 208.62 | 236.94 | 282.59 | 317.14 | 387.04 | | | | |
| | | | | | | | | | |
| 24.32 | 32.65 | 34.32 | 40.98 | 42.65 | 47.65 | | | | |
| 11.92 | 16.10 | 16.95 | 20.34 | 21.20 | 23.77 | | | | |
| 161.48 | 218.11 | 229.62 | 275.55 | 287.20 | 322.01 | | | | |
| 26.93 | 32.87 | | | | | | | | |
| 15.33 | 18.80 | | | | | | | | |
| 207.68 | 254.68 | | | | | | | | |
| 46.43 | 55.42 | | | | | | | | |
| 26.81 | 32.24 | | | | | | | | |
| 363.20 | 436.76 | | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |

energies of these electron transitions the discontinuities of the absorption on the shorter wave-length side of the main edge result. So the fine absorption structures are pure atomic. Kronig proposed the following theory: Owing to the interaction between the atoms which are distributed regularly in the substance, the range to which an electron is able to transit appears periodically in the outer field of the atom and the transitions of an electron to these ranges are the cause of the fine structures. According to this theory, therefore, the structure must depend upon the crystal form of the absorber. To test these two ideas, we investigated the appearance of the structures of two different elements which have the same crystal form and that of the structures of an element which has a different crystal form. The photograms are shown in Plate Group B. On the photographic plates we can see many black lines, and the energy differences and wave-length differences from the main edge are measured. The results are summarized in Table 3, and graphically represented in the annexed figure. In the Table, a, b, c,...mean the points where the blackening begins, i. e. the absorption ends, and a′, b′, c′,.....the points where the blackening ends, i. e. the absorption begins. The black lines near the principal edge are in general sharper than those farther from the edge as Hanawalt[1] pointed out. Owing to the diffuseness of the structure, the errors in wave-length reading were about 1 x. u. From the results obtained, we can get the following conclusions:—

(1) So far as Ni, Cu and Zn are concerned, in the structures of the pure metal and its compounds, there are no black lines which correspond to each other, i. e. the structures are not alike in appearance. This is contrary to the result of Lindsay's early investigation on metallic Fe and its compounds[2].

(2) The appearance of the structure of metallic Ni is very like that of metallic Cu. We can easily point out the black lines and white lines which correspond to each other. The crystal forms of these metals are both face centred cubic lattice. Taking the grating constants of metallic Ni and Cu, 3.51 Å and 3.628 Å respectively, we calculated the product of the energy separation in volts from the main edge and the square of the grating constant for Ni and Cu. The results are tabulated in Table 4.

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1. J. D. Hanawalt: loc. cit. (the former)
2. G. A. Lindsay and H. R. Voorhees: loc. cit.

Table 4

(Energy Separation in Volts)×(Grating Constant)$^2$

| | Ni | Cu |
|---|---|---|
| a | 191.95 | 126.62 |
| a′ | 420.61 | 411.85 |
| b | 531.80 | 485.03 |
| b′ | 996.45 | 914.79 |
| c | 1230.04 | 1130.52 |
| c′ | 1695.74 | 1713.61 |
| d | 2107.97 | 1932.90 |
| d′ | 2465.13 | 2373.31 |
| e | 2643.65 | 2596.15 |
| e′ | 2763.89 | 2745.94 |
| f | 3124.38 | 3118.70 |
| f′ | 3852.00 | 3719.56 |
| g | 4346.04 | 4174.32 |
| g′ | 5213.99 | 5094.37 |

In this table we see that the products are nearly of the same order in Ni and Cu for corresponding lines, but not so good as the data Lindsay[1] obtained for K compounds. Moreover we can not fail to see that the energy separations of each corresponding black line are generally larger for Ni than for Cu.

(3) We can not point out corresponding lines in metallic Cu or Ni and metallic Zn.

(4) While the structures of metallic Ni and Cu are very similar in appearance, those of their oxides NiO, CuO are quite different, so we can not point out any corresponding lines in them. The appearance of the ZnO edge is also different from those of CuO and NiO. Here we must call attention to the fact that the crystal forms of NiO, CuO and ZnO are all different.

(5) Comparing the structures of the Zn edge for zincite and zinc blende, we can not point out corresponding lines in them. The appearance of the Zn edge for wurtzite seems to be like that of zincite in some respects and to zinc blende in other respects. The crystal forms of zincite and wurtzite are both hexagonal and that of zinc

1. G. A. Lindsay: loc. cit.

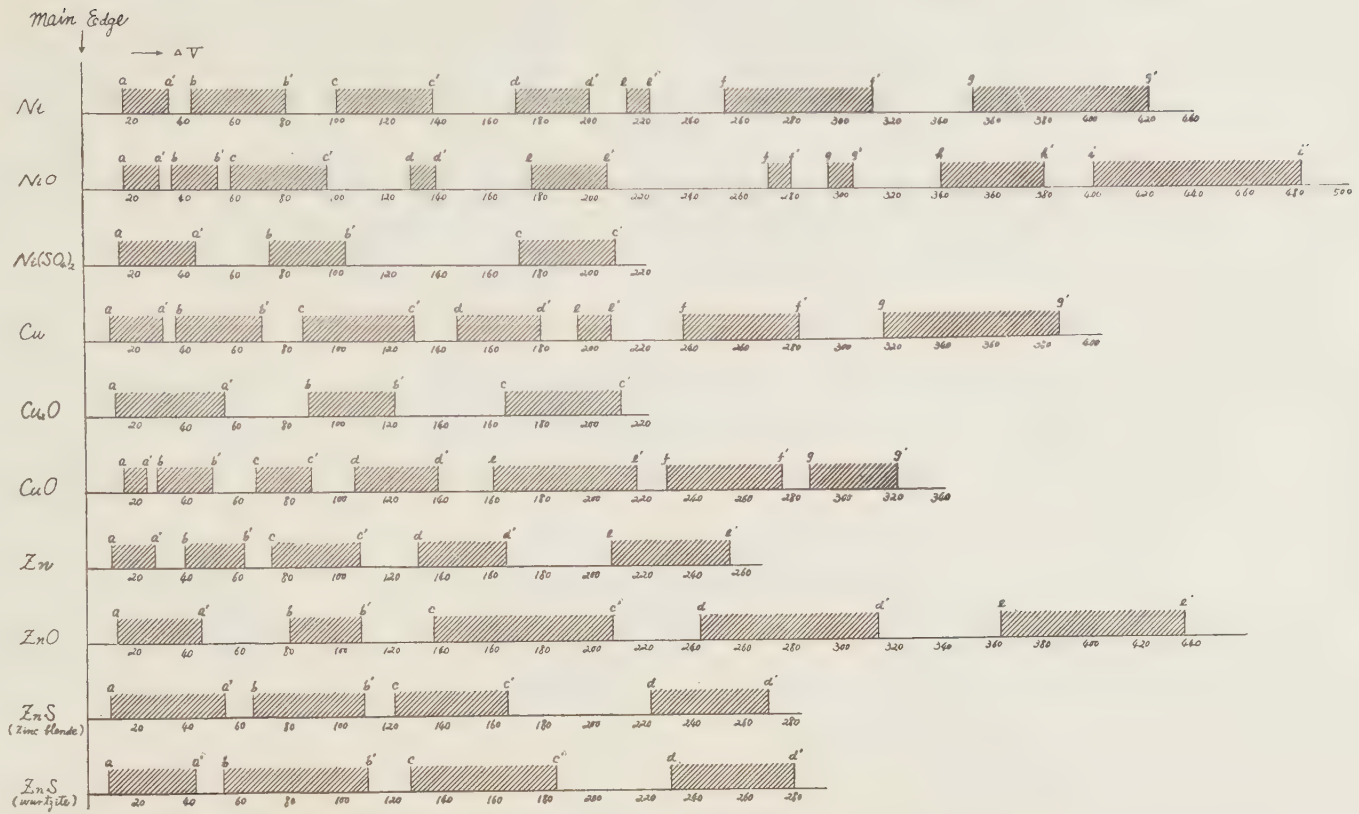
blende is cubic. In this connection we must note that wurtzite crystals are always mixed with more or less zinc blende crystals. At any rate, we can conclude that metallic zinc, zincite and zinc blende are different in appearance.

These facts seem to support Kronig's idea rather than the idea of simultaneous transitions of many electrons. But the problem " What is the origin of these structures ? " can only be solved by farther investigation.

In conclusion, we wish to express our thanks to Prof. Matsubara of the Mineralogical Institute for his kindness of giving us the sample of wurtzite crystal.

## Figure

Graphical Representation of the Energy Separations (in volts) of the Fine Structures from the Main Edge.



## Plate


Group A
Ni
NiO
Ni
Cu
$Cu_2O$
Cu
Cu
CuO
Cu
Zn
ZnO
Zn
Group B
Ni
NiO
$Ni(SO_4)_2$
Cu
$Cu_2O$
CuO
Zn
ZnS
(Zinc Blende)
ZnS
(Wurtzite)

# Electrolytic Deposition of Zinc from Acid Solutions

By

**Hisashi Kiyota**

(Received July 18, 1932)

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There are a great many works dealing with electrolytic deposition of zinc from various acid solutions, but none of the methods hitherto proposed could be regarded as perfect. As the chief difficulty in zinc electrolysis was thought to lie in the specific property of zinc of forming a spongy deposit, an attempt was made, in this investigation, to ascertain how far this difficulty might be overcome by controlling the current density on the one hand and the concentration of acid on the other. It soon became clear that, in order to obtain reliable results, the current density must be restricted within certain limits which vary according to the concentration of acid. In an acetic acid solution the limits within which the current density must be restricted are comparatively wide, while in a sulphuric acid solution they are so narrow that exact working is hardly practicable.

The zinc sulphate used in the experiment was prepared either by dissolving pure zinc obtained from E. Merck in dilute sulphuric acid so as to make the concentration of free acid in the resulting zinc sulphate solution nearly 1/10 normal, or by first neutralizing the acid in the zinc sulphate solution with caustic soda and then adding an amount of acetic acid properly calculated to make its concentration in the solution 1/10 normal.

Throughout all the experiments a platinum basin was always employed as the cathode, and in order to know what kind of results would be attainable, when the methods previously known were worked with this cathode, a series of experiments was performed according to the

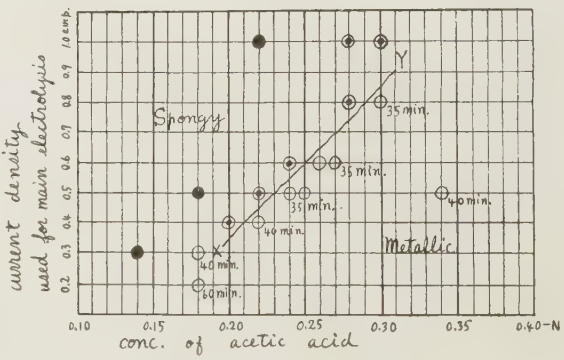
methods given by F. Spitzer[1], A. Fischer and R. J. Boddaert[2], F. F. Exner[3], and L. H. Ingham[4]. None of these methods, however, gave satisfactory results, always producing the deposit in spongy forms, some of which were found to adhere to the cathode so loosely that even washing of it could not be effected.

A thorough revision of the electrolysis of zinc, which was thus deemed indispensable, was carried out by the present author, very minute attention being paid both to the current density for the electrolysis and to the concentration of acid in the zinc sulphate solution.

## A. Acetic Acid Solution

I. With a platinum basin of about 150 c.c. capacity previously plated with copper as the cathode, electrolysis was conducted by rotating the anode consisting of a platinum disk at the rate of about 1500 revs. per minute. As the electrolyte, a solution containing about 0.1 gram. of zinc, 6 grams. of crystalline sodium acetate, some sodium sulphate (below 0.02 normal) and different quantities of acetic acid in 125 c.c. was taken, and this was electrolysed by passing a current of comparatively small density (main electrolysis), till the electrolyte ceased to give the potassium ferrocyanide reaction for zinc and then raising the current density to about 3 amperes (final electrolysis) for about 10 minutes. The results are shown in Fig. 1.

Fig. 1




Generally speaking, the region lying below the line XY gave the zinc deposit in a metallic form, while that lying above the line produced the spongy

1. F. Spitzer; Zeitschr, f. Elektrochem., **11** (1905), 404.
2. A. Fischer and R. J. Boddaert; Zeitschr, f. Elektrochem., **10** (1904), 946.
3. F. F. Exner; Journ. Am. Chem. Soc., **25** (1903), 899; Chemisches Zentralblatt, **2** (1903), 1210.
4. L. H. Ingham; Journ. Am. Chem. Soc., **26** (1904), 1270; Chemisches Zentralblatt, **2** (1904), 1758.

or powdery deposit. The cases in which zinc was electrolysed as a deposit with metallic lustre and bluish white colour are marked with ○, and those, in which the results were tolerably good, only the last small portion of the deposit being produced in a spongy state, are marked ⊙. The third mark ● stands for the worst cases which could, by no means, be used for analytical purposes. The time required for complete deposition was 35–60 minutes and is given in the figure under the mark ○.

II. In the next series of experiments, the current density for the main electrolysis was kept at 0.5 ampere, and the concentration of acetic acid and the current density for the final electrolysis were changed. The results are shown in table I (No. 1—No. 18) and Fig. 2.

Table I

A

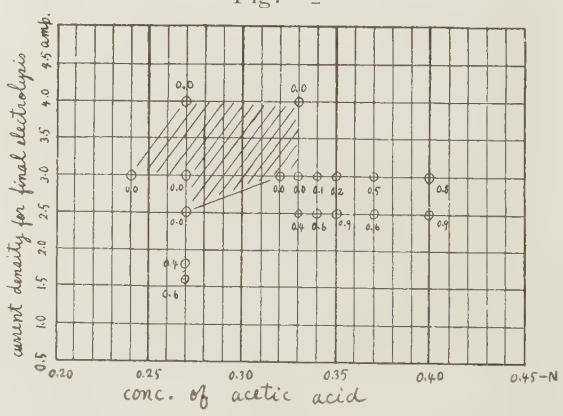
| No. | ELECTROLYTE | | | | |
|---|---|---|---|---|---|
| | Zn mgms. | Conc. of acetic acid (Normality) | $CH_3CO_2Na \cdot 3H_2O$ gms. | Conc. of $Na_2SO_4$ (Normality) | Volume c.c. |
| 1 | 100.6 | 0.27 | 6 | 0.02 | 125 |
| 2 | „ | „ | „ | „ | „ |
| 3 | „ | „ | „ | „ | „ |
| 4 | „ | „ | „ | „ | „ |
| 5 | „ | „ | „ | „ | „ |
| 6 | „ | 0.40 | „ | „ | „ |
| 7 | „ | 0.37 | „ | „ | „ |
| 8 | „ | 0.35 | „ | „ | „ |
| 9 | „ | 0.34 | „ | „ | „ |
| 10 | „ | 0.33 | „ | „ | „ |
| 11 | „ | 0.40 | „ | „ | „ |
| 12 | „ | 0.37 | „ | „ | „ |
| 13 | „ | 0.35 | „ | „ | „ |
| 14 | „ | 0.34 | „ | „ | „ |
| 15 | „ | 0.33 | „ | „ | „ |
| 16 | „ | 0.32 | „ | „ | „ |
| 17 | „ | 0.24 | „ | „ | „ |
| 18 | „ | 0.33 | „ | „ | „ |

Table I

B

| No. | Main Electrolysis | | | | Final electrolysis (About 10 minutes) | | | Error mgms. |
|---|---|---|---|---|---|---|---|---|
| | Current density $ND_{100}$ amp. | Volts | Temp. | Time mins. | Current density $ND_{100}$ amp. | Volts | Final temp. | |
| 1 | 0.5 | 6.1–6.0 | 16–24° | 55 | 1.6 | 10.4– 8.8 | 38° | −0.6 |
| 2 | „ | 6.2–6.2 | 17–24° | 45 | 1.8 | 11.6–10.4 | 40° | −0.4 |
| 3 | „ | 6.1–6.1 | 18–24° | „ | 3.0 | 15.6–13.4 | 53° | −0.0 |
| 4 | „ | 6.2–6.1 | 15–23° | „ | 2.5 | 13.8–11.6 | 45° | −0.0 |
| 5 | „ | 6.1–6.2 | 15–23° | „ | 4.0 | 19.6–15.4 | 73° | −0.0 |
| 6 | „ | 6.2–6.0 | 14–24° | „ | 2.5 | 13.6–11.4 | 43° | −0.9 |
| 7 | „ | —— | —— | „ | „ | —— | —— | −0.6 |
| 8 | „ | —— | —— | „ | „ | —— | —— | −0.9 |
| 9 | „ | —— | —— | „ | „ | —— | —— | −0.6 |
| 10 | „ | 6.2–6.1 | 17–23° | „ | „ | 13.4–11.2 | 45° | −0.4 |
| 11 | „ | 6.0–6.1 | 16–22° | 40 | 3.0 | 16.2–13.0 | 52° | −0.8 |
| 12 | „ | —— | —— | 45 | „ | —— | —— | −0.5 |
| 13 | „ | —— | —— | „ | „ | —— | —— | −0.2 |
| 14 | „ | —— | —— | 40 | „ | —— | —— | −0.1 |
| 15 | „ | 6.0–6.0 | 17–24° | 45 | „ | 16.6–13.2 | 54° | −0.0 |
| 16 | „ | —— | —— | „ | „ | —— | —— | −0.0 |
| 17 | „ | 6.1–6.0 | 17–24° | „ | „ | 16.4–13.2 | 57° | −0.0 |
| 18 | „ | 6.1–6.1 | 17–23° | 40 | 4.0 | 19.8–15.0 | 72° | −0.0 |

Fig. 2




In the region marked by oblique lines the zinc was found to be deposited quantitatively. The error, which was always negative, is given in the figure by numbers which represent milligrams.

Combining the results of the above two series of experiments we may conclude that the best conditions for electrolysing zinc from an acetic acid solution are as follows:

Concentration of acetic acid: 0.27–0.33 normal
Current density for main electrolysis: 0.5–0.6 ampere
„ „ „ final electrolysis: 3–4 amperes

III. In the foregoing two series of experiments the amount of zinc for each analysis was always about 0.1 gram. A third series of experiments was now undertaken to see how the electrolysis would be effected by the concentration of zinc in the electrolyte, and to learn how the concentration of the acid should be changed according to the amount of zinc. As will be seen from the results shown in Table II, the suitable normality of acid for electrolysing 0.5 gram of zinc was found to be between 0.14 and 0.21. In a more diluted acid solution the zinc crystals became somewhat coarse. When the amount of zinc was 0.3 gram the best result was produced by maintaining the normality of acid at 0.21—0.27 normal. With a solution in which the amount of zinc present was as small as 0.001 gram in 125 c.c. the cathode should previously be plated with zinc, otherwise, not only is the current yield very much lowered, but complete deposition of zinc becomes unattainable. The results are shown in Table II.

Table II

A

| No. | ELECTROLYTE | | | | |
|---|---|---|---|---|---|
| | Zn mgms. | Conc. of acetic acid (Normality) | $CH_3CO_2Na \cdot 3H_2O$ gms. | Conc. of $Na_2SO_4$ (Normality) | Volume c.c. |
| 1 | 500.0 | 0.13 | 6 | 0.02 | 125 |
| 2 | „ | „ | „ | „ | „ |
| 3 | „ | 0.15 | „ | „ | „ |
| 4 | „ | „ | „ | „ | „ |
| 5 | „ | 0.21 | „ | „ | „ |
| 6 | „ | „ | „ | „ | „ |
| 7 | „ | 0.15 | „ | „ | „ |
| 8 | „ | 0.21 | „ | „ | „ |
| 9 | 300.0 | „ | „ | „ | „ |
| 10 | „ | „ | „ | „ | „ |
| 11 | „ | 0.27 | „ | „ | „ |
| 12 | „ | „ | „ | „ | „ |
| 13 | 1.0 | 0.30 | „ | „ | „ |
| 14 | „ | 0.36 | „ | „ | „ |
| 15 | „ | „ | „ | „ | „ |

Table II
B

| No. | Main Electrolysis | | | | Final Electrolysis (10 minutes) | | | Error mgms. |
|---|---|---|---|---|---|---|---|---|
| | Amp. ($ND_{100}$) | Volts | Temp. | Time mins. | Amp. ($ND_{100}$) | Volts | Final temp. | |
| 1 | 0.5 | —— | —— | 80 | 3.0 | —— | —— | +0.1 |
| 2 | 0.6 | —— | —— | 75 | „ | —— | —— | −0.0 |
| 3 | 0.5 | —— | —— | 75 | „ | —— | —— | −0.0 |
| 4 | „ | —— | —— | 80 | „ | —— | —— | −0.0 |
| 5 | „ | 5.7−5.7 | 17−24° | 80 | „ | 15.4−12.6 | 58° | +0.1 |
| 6 | 0.6 | 6.0−6.0 | 17−28° | 65 | „ | 16.0−11.4 | 55° | −0.1 |
| 7 | 0.5 | 5.8−5.9 | 17−27° | 75 | 4.0 | 18.8−14.4 | 76° | +0.1 |
| 8 | „ | —— | —— | „ | „ | —— | —— | −0.0 |
| 9 | 0.6 | 6.3−6.3 | 16−23° | 50 | 3.0 | 16.2−12.0 | 53° | +0.0 |
| 10 | 0.5 | 6.0−5.9 | 17−25° | 60 | 4.0 | 20.0−14.6 | 73° | −0.0 |
| 11 | „ | —— | —— | 70 | 3.0 | —— | —— | −0.0 |
| 12 | „ | —— | —— | 60 | 4.0 | —— | —— | +0.1 |
| 13 | „ | —— | —— | 0 | 3.0 | 17.8−12.6 | 52° | −0.0 |
| 14 | „ | 6.1−6.1 | 18−25° | 15 | „ | —— | —— | −0.1 |
| 15 | „ | —— | —— | 0 | 3.5 | —— | —— | −0.0 |

Table III
A

| No. | ELECTROLYTE | | | | |
|---|---|---|---|---|---|
| | Zn mgms. | Conc. of acetic acid (Normality) | Acetate | Other Salts | Volume c.c. |
| 1 | 500.0 | 0.15 | $CH_3CO_2Na \cdot 3H_2O$ 6 gms. | $Na_2SO_4$ 0.15−N | 125 |
| 2 | „ | „ | „ | „ | „ |
| 3 | „ | „ | $CH_3CO_2NH_4$ 3.4 gms. | $Na_2SO_4$ 0.02−N | „ |
| 4 | 100.6 | 0.33 | $CH_3CO_2Na \cdot 3H_2O$ 6 gms. | $NaNO_3$ 0.03−N<br>$Na_2SO_4$ 0.02−N | „ |
| 5 | „ | „ | „ | $NaNO_3$ 0.1−N<br>$Na_2SO_4$ 0.02−N | „ |
| 6 | „ | „ | „ | NaCl 0.15−N<br>$Na_2SO_4$ 0.02−N | „ |
| 7 | 105.4 | „ | „ | NaCl 0.03−N<br>$Na_2SO_4$ 0.02−N | „ |
| 8 | „ | „ | „ | „ | „ |

Table III

B

| No. | Main Electrolysis | | | | Final Electrolysis (10 minutes) | | | Error mgms. |
|---|---|---|---|---|---|---|---|---|
| | Amp. ($ND_{100}$) | Volts | Temp. | Time mins. | Amp. ($ND_{100}$) | Volts | Final temp. | |
| 1 | 0.6 | 6.0—6.0 | 17°—24° | 70 | 3.0 | 14.4—11.2 | 48° | —0.0 |
| 2 | 0.5 | —— | —— | 85 | „ | 14.2—10.2 | 50° | —0.1 |
| 3 | „ | 5.7—5.5 | 19 —25° | 80 | 1.5 | 8.5— 8.1 | 34° | —0.5 |
| 4 | „ | 5.3—5.7 | 18°—27° | 110 | 3.0 | 14.8—11.6 | 53° | +0.1 |
| 5 | „ | —— | —— | 300 | | | | |
| 6 | „ | 5.3—5.2 | 17°—24° | 50 | 3.0 | 12.4—10.8 | 50° | —1.5 |
| 7 | „ | 5.5—5.7 | 18°—26° | 55 | „ | 15.6—12.8 | 53° | —0.6 |
| 8 | „ | —— | —— | 50 | 4.5 | 19.0—14.0 | 78° | —0.1 |

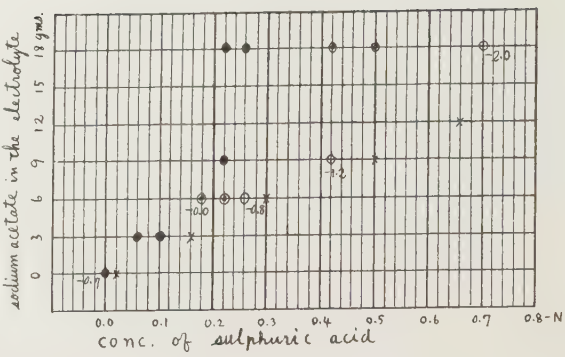
IV. The influence of such substances as sodium sulphate, ammonium sulphate, ammonium acetate, sodium chloride and sodium nitrate on zinc deposition was investigated and the results tabulated in Table III were obtained. The presence of sodium sulphate, ammonium sulphate and ammonium acetate has no significant bad influence, when their dilution is lower than 0.15 normal. Nitrates greatly retard deposition of the metal and tend to make the zinc deposit spongy. The effect of chlorides is not nearly so bad as that of nitrates, but still they often become a cause of negative error.

## B. Sulphuric Acid Solution

Electrolysis of a sulphuric acid solution containing about 0.1 gram of zinc, and from 0 to 18 grams of sodium acetate was carried out nearly in the same manner as in the electrolysis of the acetic acid solution. The current density for the main electrolysis was maintained between 0.4–0.5 ampere, and that for the final electrolysis at 3 amperes, and the electrolytic bath was cooled by a current of cold water.

So far as the present experiments are concerned, electrolytic deposition of zinc from a sulphuric acid solution could not be achieved with satisfactory results even by controlling the current density and the concentration of the acid in several ways. In Fig. 3 the results obtained by passing a current of 0.5 ampere for main electrolysis are shown. The cases in which comparatively good results were obtained are shown by the mark ○, while the mark ⊙ stands for those which

Fig. 3




were not so good, and ● for the worst cases. It may thus be concluded that for zinc electrolysis in a sulphuric acid solution, the acidity of the bath, which must contain about 0.1 gram of zinc and 6 grams of sodium acetate in 125 c.c., should be kept between 0.14–0.26 normal, and a current of 0.5 ampere should be passed for the main electrolysis.

Experiments were next conducted with the bath containing 5, 6 or 7 grams of sodium acetate, and a current of 0.4 ampere for the main electrolysis. In these cases too, the solution containing 6 grams of sodium acetate was found to give the best results if the concentration of sulphuric acid were kept at 0.18 normal, as is seen in Table IV and Fig. 4.

Table IV

A

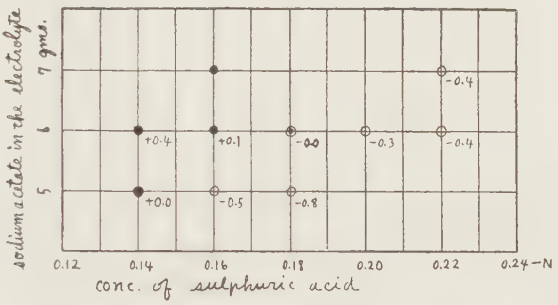
| No. | ELECTROLYTE | | | |
|---|---|---|---|---|
| | Zn mgms. | $CH_3CO_2Na \cdot 3H_2O$ gms. | Conc. of $H_2SO_4$ (Normality) | Volume c.c. |
| 1 | 99.9 | 6 | 0.22 | 125 |
| 2 | „ | „ | 0.20 | „ |
| 3 | „ | „ | 0.18 | „ |
| 4 | „ | „ | 0.16 | „ |
| 5 | „ | „ | 0.14 | „ |
| 6 | „ | „ | 0.22 | „ |
| 7 | „ | 5 | 0.18 | „ |
| 8 | „ | „ | 0.16 | „ |
| 9 | „ | „ | 0.14 | „ |
| 10 | „ | 7 | 0.22 | „ |

Table IV

B

| No. | Main Electrolysis | | | | Final Electrolysis (10 minutes) | | | Error mgms. |
|---|---|---|---|---|---|---|---|---|
| | Amp. ($ND_{100}$) | Volts | Temp. | Time mins. | Amp. ($ND_{100}$) | Volts | Final temp. | |
| 1 | 0.4 | 5.3—5.2 | 15°—21° | 45 | 3 | 15.4—15.2 | 29° | —0.4 |
| 2 | „ | | 15 —21° | „ | „ | | 25° | —0.3 |
| 3 | „ | | 14 —21° | 55 | „ | | 29° | —0.0 |
| 4 | „ | | 18 —24° | 85 | „ | | 28° | +0.1 |
| 5 | „ | 5.2—5.2 | 17 —22° | 55 | „ | 15.6—15.2 | 26° | +0.4 |
| 6 | „ | | 16 —23° | 60 | 3.5 | 18.4—17.8 | 28° | —0.4 |
| 7 | „ | 5.4—5.3 | 17 —22° | 45 | 3 | 16.8—16.4 | 26° | —0.8 |
| 8 | „ | | 17 —20° | 60 | „ | | 28° | —0.5 |
| 9 | „ | | 17 —24° | „ | „ | | 27° | +0.0 |
| 10 | „ | 5.0—5.0 | 18 —20° | 45 | „ | 15.2—14.8 | 28° | —0.4 |

Fig. 4




## Summary

1) All the methods hitherto proposed for electrolysing zinc from an acid solution were experimentally confirmed to give no satisfactory results, when a Classen's electrode is employed.

2) The best conditions necessary for producing zinc in a metallic form on Classen's electrode from an acid solution quantitatively were sought by controlling the current density on the one hand and the concentration of the acid on the other.

3) Though in the case of sulphuric acid solutions it was hardly possible to find any conditions under which zinc doposition could be worked with complete safety, a very satisfactory and reliable method was found with acetic acid solutions.

4) In carrying out the electrolysis, a current of 0.5–0.6 ampere should first be passed, till the solution ceases to give the potassium ferrocyanide reaction for zinc, and then the current density should be raised to 3–4 amperes for a further 10 minutes. The faster the anode is rotated the better is the deposit produced.

5) The concentration of acetic acid should be adjusted according to the amounts of zinc present in the following way:

| | |
|---|---|
| For 0.5 gram Zn | 0.15–0.21 normal |
| „ 0.3 „ „ | 0.21–0.27 „ |
| „ 0.1 „ „ | 0.27–0.33 „ |

6) The duration of the electrolysis varies from 35 minutes to 80 minutes according to the amounts of zinc, thus—

| | |
|---|---|
| 0 5 gram Zn | 65–80 min. |
| 0.3 „ „ | 50–60 „ |
| 0.1 „ „ | 35–40 „ |

7) The presence of such salts as sodium sulphate and ammonium sulphate does not interfere with the electrolysis, if their concentration is below 0.15 normal. Nitrates and chorides must not be present in the bath.

8) Under the conditions above stated the zinc deposit is obtained as a smooth metallic coating, so that the electrode thus coated may be used directly for the next electrolytic analysis of zinc.

The author takes this opportunity of expressing his warm thanks to Professor Motooki Matsui, under whose guidance and encouragement this work was carried out.

# Experimental Studies on the Sound of a Japanese Temple-Bell ("Ōjikichō" in Myōshinji-Temple)

By

Ichiro Aoki

(Received August 3, 1932)

**Abstract**

The records of the sound waves of a Japanese temple bell belonging to Myōshinji-Temple in Kyoto, and known by the name of "Ōjikichō", were obtained by using a Low-Hilger audiometer. Analyzing them, the writer found six partial tones of frequencies about 129, 335, 550, 700, 900, and 1250. The strike-note is the 2nd partial, whose frequency is 335. About 10 secs. after the bell is struck, all the overtones disappear and only the fundamental tone continues.

In order to study the nature of the sounds emitted by Eastern bells, the writer recorded the sound waves of a large temple-bell, known by the name of "Ōjikichō," in Myōshinji-Temple in Kyoto by using a Low-Hilger audiometer, and analyzed the curves obtained into partial sine-curves. The method of investigation in this study was nearly the same as that previously reported by the present writer in these memoirs[1].

Fig. 1

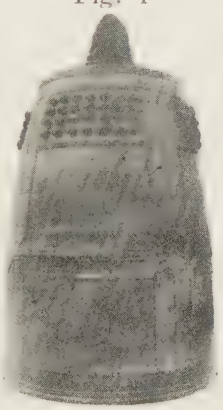
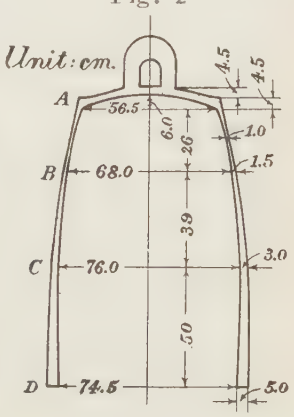


Fig. 2




The photograph and the dimensions of this bell are shown in Fig. 1 and Fig. 2. It is said that this bell was cast nearly 1300

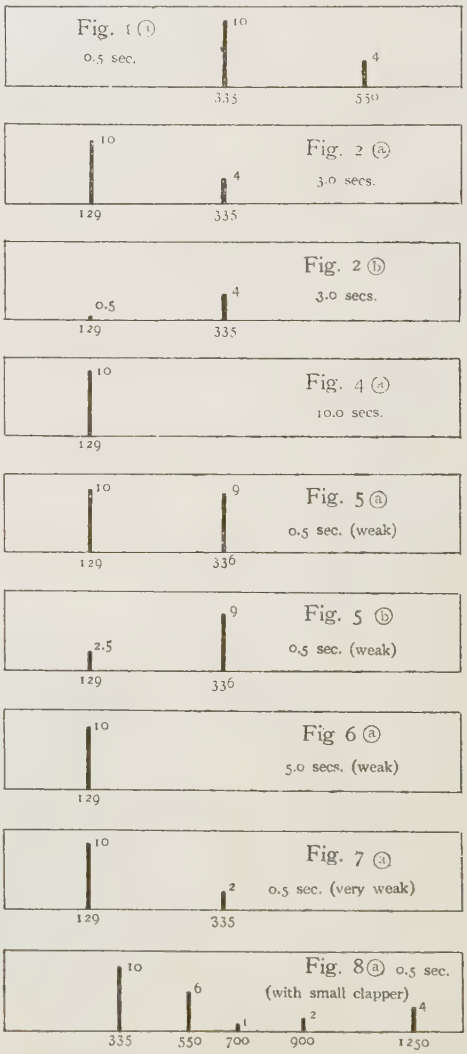
1. I. Aoki: Memoirs, Coll. of Sci. Kyoto, **14**, 213—218 (1931)

years ago. The striking seat where this bell is struck is situated somewhat higher than in ordinary Japanese bells. This is one of the characteristic features of old Japanese bells. The cross-section of this bell at the striking seat is more or less flattened elliptically, having its short radius in the direction of striking (long radius = 76 cms, short radius = 74.5 cms.). This is probably the effect of the bell's being struck for so many years. It is slightly elliptical at the mouth too (long radius = 74.5 cms., short radius = 74 cms.).

The bellstriker is a thin log of palm wood 205 cms. long and 5 cms. in radius. It is slung horizontally with ropes beside the bell. When it is desired to ring the bell, the striker is swung several times by means of another rope and finally made to give an impulse to the bell.

The records of the sounds are shown in the plate. Fig. 1–Fig. 4 were obtained by striking the bell somewhat strongly and changing the interval of time between the striking of the bell and the opening of the shutter of the camera. The horn of the recording apparatus was used to receive the sound in all cases, except that recorded in Fig. 1. Fig. 5 and Fig. 6 were obtained by striking the bell somewhat weakly, and Fig. 7 by striking it very weakly. Fig. 8 shows the record obtained when the bell was struck with a very small hand clapper.

The parts marked a, b in



these curves were analyzed by the method of periodogram analysis, and the forgoing diagram was obtained.

The letters ⓐ, ⓑ in this diagram correspond to the portions a, b in the plate. As is shown in this diagram, this bell has 6 partial tones, whose frequencies are 129, 335, 550, 700, 900, 1250 respectively. Among these partials, the 4th one (frequency=700) is very weak and has very small amplitude, and it is not clear whether this tone really exists or not. In Fig. 1 and Fig. 8 the fundamental tone does not appear while the 2nd partial is highly predominating, which shows that the strike-note of this bell is the 2nd partial. This strike-note has 78 beats per sec., from which we see that it consists of two tones, whose frequencies are 296 and 374. About 10 secs. after the bell is struck, all the over-tones vanish, and only the fundamental tone continues, remaining for about 40 secs. with 5 beats per sec. Fig. 8 shows that when the bell is struck with a small clapper there appear still higher over-tones and that the fundamental tone does not appear at all.

The above results need some corrections due to the proper oscillations of the various parts of the recording instrument. It was found that the ratios of sensitiveness of diaphragm for 129, 335, 550, 700, 900, 1250 are 1, 3, 3, 3, 2, 1 respectively. Therefore the amplitudes of 129 and 1250 must be magnified about 3 times, and that of 900 about 1.5 times to get the right amplitudes.

In conclusion the writer wishes to express his great gratitude to Prof. K. Tamaki for his guidance and instruction, and to the staff of Myōshinji-Temple for the permission to use the bell for this study.

Fig. 1 0.5 sec. after it is struck.

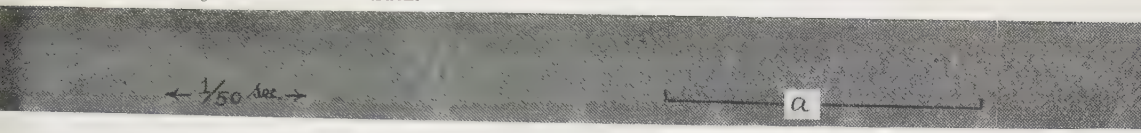



Fig. 2 3.0 secs.

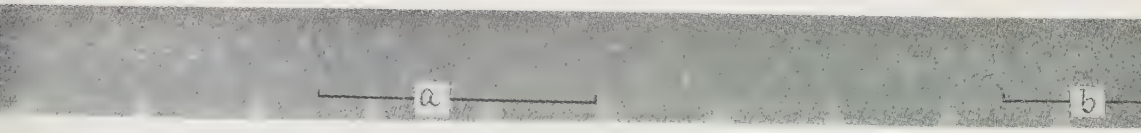



Fig. 3 6.0 secs.

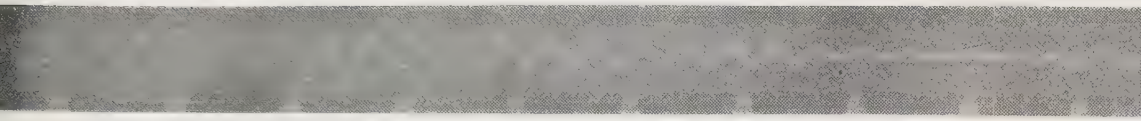


Fig. 4 10.0 secs.

Fig. 5 0.5 sec.

Fig. 6 5.0 secs.

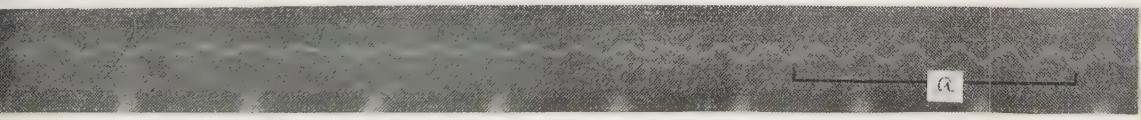
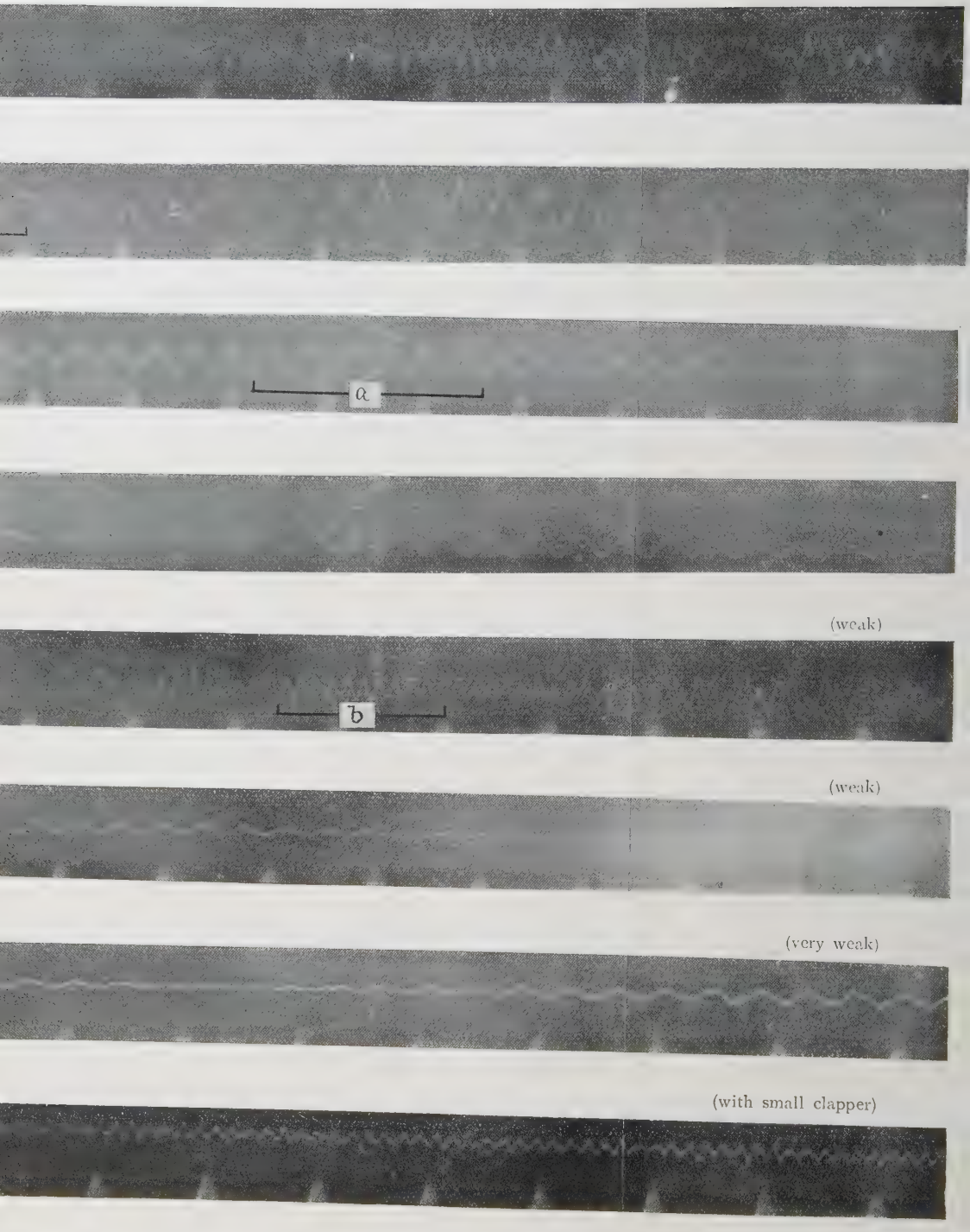



Fig. 7 0.5 sec.

Fig. 8 0.5 sec.


a
(weak)
b
(weak)
(very weak)
(with small clapper)

# A Theory of the Vibration of Japanese Hanging Bells

By

**Keiji Yamashita**

(Received August 3, 1932)

**Abstract**

The frequencies of the vibration of the Japanese hanging bell are calculated on the assumption that it is a circular cylinder with a hemispherical cap and no line traced upon the middle surface of the shell undergoes extension when the bell is sounding. It is found that the frequencies of the partial tones of a Japanese bell, of which the Poisson's ratio is 1/3 and the ratio of the length of the cylindrical part to its radius is 3/2, are in the ratios 359 : 981 : 1847 : . . . . .

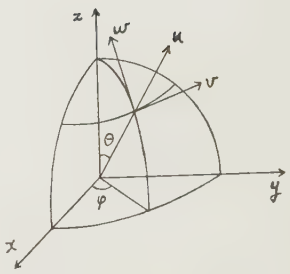
The shape of the Japanese bell may roughly be represented by a circular cylinder with a hemispherical cap. But its thickness is not uniform everywhere, being very thin at the portion where the cylindrical part changes to the spherical form and very thick at the edge as well as at the top of the bell. Since an exact calculation is indeed scarcely to be hoped for, we assume, in the present paper, that the thickness of the shell is uniform throughout the bell. The vibration of a spherical shell[1] and of a cylindrical shell[2] are treated by Lord Rayleigh on the assumption that the shell is deformed by pure bending. Following Lord Rayleigh, we assume that any line on the middle surface of the shell undergoes no extension when the bell is sounding.

Let $r$, $\theta$, $\varphi$ be the spherical polar coordinates of any point of a hemispherical shell in the equilibrium state, and let $(u, v, w)$ represent

1. Lord Rayleigh, Lond. Math. Soc. Proc. **13**, 4–6 (1881); Scientific Papers, vol. 1, pp. 551–562.

2. Lord Rayleigh, Roy. Soc. Proc., **45**, 105–123 (1888); Scientific Papers, vol. 3, pp. 217–232.

the displacement of that point in any state of vibration, $u$ being the component along the radius vector, $v$ that along the tangent to the parallel in the increasing direction of $\varphi$, and $w$ that along the tangent to the meridian in the decreasing direction of $\theta$. Then the most general possible forms for $u$, $v$, $w$, when the boundaries of the shell are two circles of latitude and the displacement is that of pure bending, are given by[1]




$$\left.\begin{aligned} u &= -\sum\{(n+\cos\theta)A_n\tan^n\frac{\theta}{2}\cos(n\varphi+\alpha_n) \\ &\qquad -(n-\cos\theta)B_n\cot^n\frac{\theta}{2}\cos(n\varphi+\beta_n)\}, \\ v &= \sin\theta\sum\{A_n\tan^n\frac{\theta}{2}\sin(n\varphi+\alpha_n) - B_n\cot^n\frac{\theta}{2}\sin(n\varphi+\beta_n)\}, \\ w &= -\sin\theta\sum\{A_n\tan^2\frac{\theta}{2}\cos(n\varphi+\alpha_n) + B_n\cot^n\frac{\theta}{2}\cos(n\varphi+\beta_n)\}; \end{aligned}\right\} \quad (1)$$

where $A_n$ and $B_n$ are functions of time $t$, $\alpha_n$ and $\beta_n$ pure constants, and the summation is taken with possible integral values of $n$ from zero to infinity. But, since the terms for $n=0$ and $n=1$ correspond to the displacements of the shell when it moves as a rigid body, they may be omitted from the summation. Moreover to apply equations (1) to a hemispherical shell, since the displacement at the pole $\theta=0$ must be finite, we must reject the terms containing $\cot^n\frac{\theta}{2}$. Thus we get

$$\left.\begin{aligned} u &= -\sum(n+\cos\theta)A_n\tan^n\frac{\theta}{2}\cos(n\varphi+\alpha_n), \\ v &= \sin\theta\sum A_n\tan^n\frac{\theta}{2}\sin(n\varphi+\alpha_n), \\ w &= -\sin\theta\sum A_n\tan^n\frac{\theta}{2}\cos(n\varphi+\alpha_n). \end{aligned}\right\} \quad (2)$$

Next let $a$, $\varphi$, $z$ be the cylindrical coordinates of any point on a circular cylinder of radius $a$ and $u$, $v$, $w$ be the components of dis-

1. A. E. H. Love, Math. Theory of Elasticity, 4th ed., p. 508.

placement in the directions of increase of $a$, $\varphi$ and $z$ respectively. Then for a circular cylinder of finite length, when the displacement is restricted to pure bending, the most general possible forms for $u$, $v$ ,$w$ are given by[1]

$$\left.\begin{aligned} u &= \sum n\{A'_n \sin(n\varphi+\alpha_n') + B_n' z\sin(n\varphi+\beta_n')\},\\ v &= \sum\{A_n' \cos(n\varphi+\alpha_n') + B'_n z\cos(n\varphi+\beta'_n)\},\\ w &= -\sum \frac{a}{n} B_n' \sin(n\varphi+\beta_n'), \end{aligned}\right\} \qquad (3)$$

where $A_n'$ and $B_n'$ are functions of $t$, and $\alpha_n'$ and $\beta_n'$ are pure constants.

If we consider the bell as made up by the hemisphere being connected with the cylinder, as its cap, since the displacements given by (2) and (3) must be equal at the connecting plane, which may be taken as $z=0$ passing through the center of the hemisphere, we get

$$\left.\begin{aligned} nA'_n \sin(n\varphi+\alpha_n') &= -nA_n\cos(n\varphi+\alpha n),\\ A_n'\cos(n\varphi+\alpha_n') &= A_n\sin(n\varphi+\alpha_n),\\ -\frac{a}{n}B_n'\sin(n\varphi+\beta_n') &= -A_n\cos(n\varphi+\alpha_n), \end{aligned}\right\}$$

or

$$\left.\begin{aligned} \alpha_n' &= \frac{\pi}{2}+\alpha_n, & A_n' &= -A_n,\\ \beta_n' &= \frac{\pi}{2}+\alpha_n, & B_n' &= \frac{n}{a}A_n. \end{aligned}\right\} \qquad (4)$$

Substituting these values of $A_n'$, $B_n'$ $\alpha_n'$, $\beta_n'$ given by (4) in (3), we obtain

$$\left.\begin{aligned} u &= -\sum n\left(1-\frac{n}{a}z\right)A_n\cos(n\varphi+\alpha_n),\\ v &= \sum\left(1-\frac{n}{a}z\right)A_n\sin(n\varphi+\alpha_n),\\ w &= -\sum A_n\cos(n\varphi+\alpha_n). \end{aligned}\right\} \qquad (5)$$

In order to calculate the frequencies of vibration of the bell, first let us obtain its kinetic and potential energies. Let $\rho$ be the density

1. A. E. H. Love, loc. cit. p. 506.

of the material and $2h$ be the thickness of the shell. Then the kinetic energy per unit area of the shell is evidently given by

$$\rho h\left\{\left(\frac{\partial u}{\partial t}\right)^2+\left(\frac{\partial v}{\partial t}\right)^2+\left(\frac{\partial w}{\partial t}\right)^2\right\}.$$

If the length of the cylindrical part is $l$, its kinetic energy $T_c$ is

$$T_c=\int_{-l}^{0}\int_{0}^{2\pi}\rho h\left\{\left(\frac{\partial u}{\partial t}\right)^2+\left(\frac{\partial v}{\partial t}\right)^2+\left(\frac{\partial w}{\partial t}\right)^2\right\}ad\varphi dz.$$

When the values of $u$, $v$, $w$ of (5) are substituted in the above equation, all the terms containing products of sines or cosines with different values of $n$ vanish in the integration with respect to $\varphi$, as do also those which contain $\cos(n\varphi+\alpha_n)\sin(n\varphi+\alpha_n)$. Accordingly

$$T_c=\pi\rho alh\sum\left\{(n^2+2)+(n^2+1)\left(1+\frac{1}{3}\frac{nl}{a}\right)\frac{nl}{a}\right\}\left(\frac{dA_n}{dt}\right)^2. \quad (6)$$

The potential energy of bending per unit area of the cylindrical shell is[1]

$$\frac{1}{2}D\{k^2+2(1-\sigma)\tau^2\}, \quad (7)$$

where $k$ and $\tau$ are given by[2]

$$k\equiv-\frac{1}{a^2}\left(\frac{\partial^2 u}{\partial\varphi^2}+u\right),$$

$$\tau\equiv\frac{1}{a}\frac{\partial}{\partial z}\left(v-\frac{\partial u}{\partial\varphi}\right),$$

and $D$ is the flexural rigidity

$$D\equiv\frac{2}{3}\frac{Eh^3}{1-\sigma^2}=\frac{4}{3}\frac{\mu h^3}{1-\sigma},$$

$E$, $\sigma$, and $\mu$ being Young's modulus, Poisson's ratio, and the modulus of rigidity respectively. Using the values of (5), we get

$$k=-\frac{1}{a^2}\sum n(n^2-1)\left(1-\frac{n}{a}z\right)A_n\cos(n\varphi+\alpha_n),$$

$$\tau=\frac{1}{a^2}\sum n(n^2-1)A_n\sin(n\varphi+\alpha_n).$$

1. A. E. H. Love, loc. cit. p. 503.
2. A. E. H. Love, loc. cit. p. 507.

The potential energy $V_c$ of the cylindrical portion is obtained by integrating the expression (7) over the shell; and we get

$$V_c=\int_{-l}^{0}\int_{0}^{2\pi}\frac{1}{2}D\{k^2+2(1-\sigma)\tau^2\}a\,d\varphi\,dz$$

$$=\frac{1}{2}\frac{\pi Dl}{a^3}\sum n^2(n^2-1)^2\left\{(3-2\sigma)+\frac{nl}{a}+\frac{1}{3}\frac{n^2l^2}{a^2}\right\}A_n^2$$

$$=\frac{2}{3}\frac{\pi\mu lh^3}{(1-\sigma)a^3}\sum n^2(n^2-1)^2\left\{(3-2\sigma)+\frac{nl}{a}+\frac{1}{3}\frac{n^2l^2}{a^2}\right\}A_n^2. \quad (8)$$

The kinetic enegy $T_s$ and the potential energy $V_s$ of the hemispherical portion are given by[1]

$$T_s=\pi\rho a^2h\sum\left(\frac{dA_n}{dt}\right)^2\int_0^{\frac{\pi}{2}}\sin\theta\{2\sin^2\theta+(n+\cos\theta)^2\}\tan^{2n}\frac{\theta}{2}d\theta,$$

$$V_s=\frac{8}{3}\frac{\pi\mu h^3}{a^2}\sum n^2(n^2-1)^2A_n^2\int_0^{\frac{\pi}{2}}\tan^{2n}\frac{\theta}{2}\frac{d\theta}{\sin^3\theta}.$$

By the transformation of the variable $1+\cos\theta=x$, we easily get the relation

$$\int_0^{\frac{\pi}{2}}\sin\theta\{2\sin^2\theta+(n+\cos\theta)^2\}\tan^{2n}\frac{\theta}{2}d\theta$$

$$=\int_1^2\{(n-1)^2+2(n+1)x-x^2\}\frac{(2-x)^n}{x^n}dx;$$

and similarly by putting $\tan\frac{\theta}{2}=x$, we get

$$\int_0^{\frac{\pi}{2}}\tan^{2n}\frac{\theta}{2}\frac{d\theta}{\sin^3\theta}=\frac{1}{4}\frac{2n^2-1}{n(n^2-1)}.$$

Hence the expressions for $T_s$ and $V_s$ become

$$T_s=\pi\rho a^2h\sum\left(\frac{dA}{dt}\right)^2\int_1^2\{(n-1)^2+2(n+1)x-x^2\}\frac{(2-x)^n}{x^n}dx, \quad (9)$$

$$V_s=\frac{2}{3}\frac{\pi\mu h^3}{a^2}\sum n(n^2-1)(2n^2-1)A_n^2. \quad (10)$$

From (7), (8), (9) and (10), we obtain

1. A. E. H. Love, loc. cit. p. 513.

$$T=\pi\rho a^2 h\sum\left[(n^2+2)\frac{l}{a}+(n^2+1)\left(1+\frac{1}{3}\frac{nl}{a}\right)\frac{nl^2}{a^2}\right.$$
$$\left.+\int_1^2\{(n-1)^2+2(n+1)x-x^2\}\frac{(2-x)^n}{x^n}dx\right]\left(\frac{dA_n}{dt}\right)^2, \qquad (11)$$

$$V=\frac{2}{3}\frac{\pi\mu h^3}{a^2}\sum n^2(n^2-1)^2\left[\frac{1}{1-\sigma}\left\{(3-2\sigma)+\frac{nl}{a}\right.\right.$$
$$\left.\left.+\frac{1}{3}\frac{n^2l^2}{a^2}\right\}\frac{l}{a}+\frac{2n^2-1}{n(n^2-1)}\right]A_n^2 \qquad (12)$$

as the total energies of the composite shell. The kinetic energy $T$ is a series of $\dot{A}_n^2$ and the potential energy $V$ is a series of $A_n^2$, so that the coefficients $A_n$ are really the normal coordinates of the system and, by substituting (11) and (12) in Lagrange's equation of motion

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{A}_n}=-\frac{\partial V}{\partial A_n},$$

it follows that $A_n$ is proportional to a simple harmonic function of the time with a frequency $p_n/2\pi$ and $p_n$ is given by

$$p_n^2=\frac{2\mu h^2}{3\rho a^4}\frac{P}{Q},$$

where

$$\left.\begin{aligned}
P\equiv{}& n^2(n^2-1)^2\left[\frac{1}{1-\sigma}\left\{(3-2\sigma)+\frac{nl}{a}\right.\right.\\
&\left.\left.+\frac{1}{3}\frac{n^2l^2}{a^2}\right\}\frac{l}{a}+\frac{2n^2-1}{n(n^2-1)}\right],\\
Q\equiv{}&(n^2+2)\frac{l}{a}+(n^2+1)\left(1+\frac{1}{3}\frac{nl}{a}\right)\frac{nl^2}{a^2}\\
&+\int_1^2\{(n-1)^2+2(n+1)x-x^2\}\frac{(2-x)^n}{x^n}dx.
\end{aligned}\right\} \qquad (13)$$

The integral

$$f(n)\equiv\int_1^2\{(n-1)^2+2(n+1)x-x^2\}\frac{(2-x)^n}{x^n}dx$$

can be evaluated for any integral value of $n$. $f(2)$, $f(3)$ and $f(4)$ have been calculated by Lord Rayleigh[1] as follows:

1. Lord Rayleigh, Scientific Papers, vol. 1, p. 557; Theory of Sound, 2nd ed., vol. 1, p. 430.

$$f(2)=1.52961,$$

$$f(3)=1.88156,$$

$$f(4)=2.29609.$$

To obtain the ratios of the frequencies of vibration of the Japanese bell, if we assume

$$\frac{l}{a}=\frac{3}{2} \qquad \text{and} \qquad \sigma=\frac{1}{3}$$

as the reasonable values, we find from (13)

$$p_2^2=\frac{2\mu h^2}{3\rho a^4}\times 12.91,$$

$$p_3^2=\frac{2\mu h^2}{3\rho a^4}\times 96.25,$$

$$p_4^2=\frac{2\mu h^2}{3\rho a^4}\times 341.10,$$

and therefore we get

$$p_2 : p_3 : p_4=\sqrt{12.91} : \sqrt{96.25} : \sqrt{341.10}$$

$$=359 : 981 : 1847$$

as the ratios of the frequencies of partial tones.

Equation (13) may be written in the form

$$p_n^2=\frac{\mu h^2}{\rho a^4}F\left(\frac{l}{a},\sigma,n\right).$$

Therefore we see that the frequencies of corresponding vibrations of similar bells made of the same material are directly proportional to their thickness and inversely to the squares of their radii. If the similarity extend also to the thickness, the frequencies are inversely proportional to their linear dimensions. Hence, if the dimensions are halved, all the tones should rise in pitch by an exact octave.

In equation (13), if we make the length $l$ infinitely small, we obtain

$$\lim_{l\to 0} p_n^2=\frac{2\mu h^2}{3\rho a^4}\frac{n(n^2-1)(2n^2-1)}{\int_1^2\left\{(n-1)^2+2(n+1)x-x^2\right\}\frac{(2-x)^n}{x^n}dx}.$$

This is exactly the same as the equation obtained by Lord Rayleigh[1] for the frequencies of vibration of a hemispherical shell. On the other hand, if we make the length $l$ of the cylinder infinitely long in comparison with the diameter, the frequencies are given by

$$\lim_{l\to\infty} p_n^2 = \frac{2\mu h^2}{3\rho(1-\sigma)a^4}\,\frac{n^2(n^2-1)^2}{n^2+1}$$
$$= \frac{Eh^2}{3\rho(1-\sigma^2)a^4}\,\frac{n^2(n^2-1)^2}{n^2+1}.$$

These are also identical with those of a cylindrical shell obtaind by Lord Rayleigh[2].

The writer's best thanks are due to Profossor K. Tamaki who suggested the investigation and gave much valuable advice and criticism.

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1. Lord Rayleigh, Scientific Papers, vol. 1, p. 557; Theory of Sound, 2nd ed., vol. 1, p. 429.

2. Lord Rayleigh, Scientific Papers, vol. 3, p. 231; Theory of Sound, 2nd ed., vol. 1, p. 417.

# On the Frequencies of the Sound emitted by Japanese Hanging Bells

By

**Keiji Yamashita** and **Ichiro Aoki**

(Received August 3, 1932)

**Abstract**

From the experimental data, of which a part is here presented, we have found that the frequencies of the partial tones of a Japanese hanging bell are nearly in the ratios

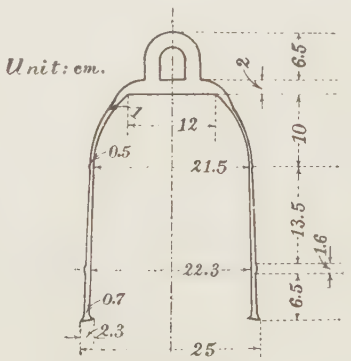
$$2^2 : 3^2 : 4^2 : 5^2 : \ldots\ldots\ldots,$$

and that the frequencies of the vibrations are inversely proportional to the linear dimensions of the bell.

The sound of a Japanese hanging fire-bell 13.5 kgms. in weight and with the dimensions shown in the figures were recorded by a Low-Hilger audiometer. Fig. 1 and Fig. 2 in the plate show the wave-forms

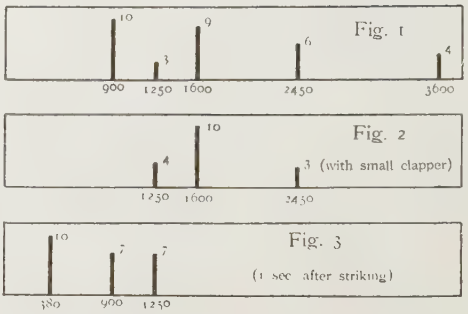
Fig. 1

Fig. 2




immediately after the bell has been struck by a wooden clapper, and Fig. 3 and Fig. 4 show the wave-forms 1 second and 2.5 seconds

respectively after the striking. Fig. 1 and Fig. 2 were recorded by the audiometer without its horn, and Fig. 3 and Fig. 4 with it. By the method of periodogram-analysis the curves in Fig. 1, Fig. 2 and Fig. 3 were analyzed and the results are shown in the annexed diagrams.




The periodogram-analysis shows that the frequencies of partial tones are

$$380,\ 900,\ 1250,\ 1600,\ 2450,\ 3600. \qquad \text{(I)}$$

If we divide these values, except 1250, by the numbers $2^2$, $3^2$, $4^2$..... respectively, we get

$$380 \div 2^2 = 85,$$
$$900 \div 3^2 = 100,$$
$$1600 \div 4^2 = 100,$$
$$2450 \div 5^2 = 98,$$
$$3600 \div 6^2 = 100.$$

We see that these quotients are approximately equal to one another, and therefore this suggests that there may be a simple and regular relation in these frequencies.

To ascertain if such a relation really exisis in other Japanese hanging bells, we shall examine the frequencies of two bells already studied by one of the writers, namely :—

$$340,\ 800,\ 1100,\ 1400,\ 1800; \qquad \text{(II)}$$
$$129,\ 335,\ 550,\ 900,\ 1250. \qquad \text{(III)}$$

The frequencies (II) are of a fire-bell[1] 19 kgms. in weight and 28 cms. in diameter, and the frequencies (III) are of a hanging bell[2] " Ōjikichō " in Myōshinji-Temple, whose diameter is about 84.5 cms. From (II) and (III), we get

$$340 \div 2^2 = 85, \qquad 129 \div 2^2 = 32,$$
$$800 \div 3^2 = 89, \qquad 335 \div 3^2 = 37,$$

1. I. Aoki, Memoirs, Coll. of Sci. Kyoto, **14**, 213—218 (1931).
2. I. Aoki, loc. cit. **15**, 311—313 (1932).

$$1400 \div 4^2 = 87, \qquad 500 \div 4^2 = 34,$$
$$900 \div 5^2 = 36,$$
$$1250 \div 6^2 = 35,$$

from which we see that the same relation also holds approximately in the frequencies of these bells.

From these facts it seems most probable that the frequencies of the partial tones of Japanese hanging bells are in the ratios

$$2^2 : 3^2 : 4^2 : 5^2 : \ldots\ldots\ldots\ldots\ldots\ldots .$$

Thus the frequencies of the partial tones follow a regular sequence, but a partial tone in (I) with frequency 1250 and two partial tones in (II) with frequencies 1100 and 1800 are not included in that sequence. It is to be supposed that these partial tones are emitted by vibrations quite different from those which emit the partial tones following the regular sequence. They are perhaps due to the vibration with nodal circles while the partial tones whose frequencies are as $2^2 : 3^2 : 4^2 : \ldots\ldots$ are due to the vibrations with nodal meridians and without any nodal circle.

In the preceding paper[1] the frequencies of the vibrations of the Japanese hanging bell were calculated by one of the writers on the assumption that it is a circular cylinder with a hemispherical cap and that no line traced upon the middle surface of the shell undergoes extension when the bell is sounding. By that calculation the frequencies of the partial tones of a Japanese hanging bell, of which the Poisson's ratio is $1/3$ and the ratio of the length of the cylindrical part to its radius is $3/2$, were found to be in the ratios $359 : 981 : 1847 : \ldots\ldots\ldots\ldots$ .

In order to compare these ratios with the experimental data, we divide the above values by $2,^2$ $3,^2$ $4,^2$ and get

$$359 \div 2^2 = 90,$$
$$981 \div 3^2 = 109,$$
$$1847 \div 4^2 = 115.$$

These quotients differ a little from one another, which is probably due to the assumption made in the theoretical investigations concerning the shape and thickness of the bell.

The diameters of the three bells (I), (II), and (III) are respectively

$$25,\ 28,\ 84.5.$$

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1. K. Yamashita, Memoirs, Coll. of Sci. Kyoto, **15**, 315—322 (1932).

Multiplying these diameters by the frequencies of their respective first partial tones, we get

$$380 \times 25 = 9500,$$
$$340 \times 28 = 9520,$$
$$129 \times 84.5 = 10900.$$

These values are approximately equal to one another, and therefore we may say that the frequencies of vibrations are inversely proportional to the linear dimensions of the bell, which is a relation obtained in the theoretical investigations.

The writers wish to express their hearty thanks to Professor K. Tamaki, to whom they are indebted for his suggestions and advice.

# Plate

Fig. 1

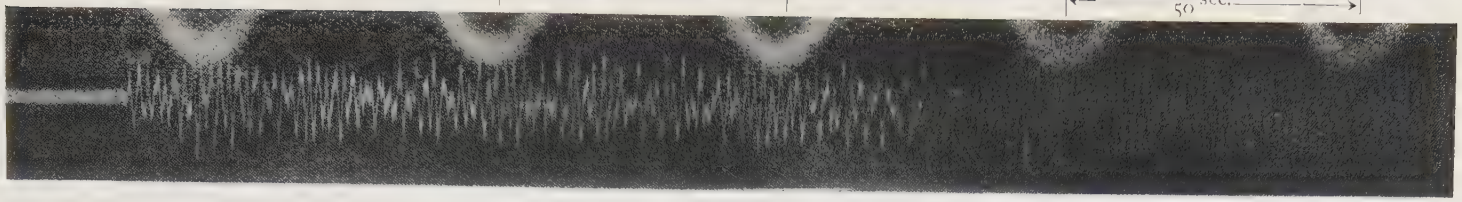



Fig. 2

Fig. 3

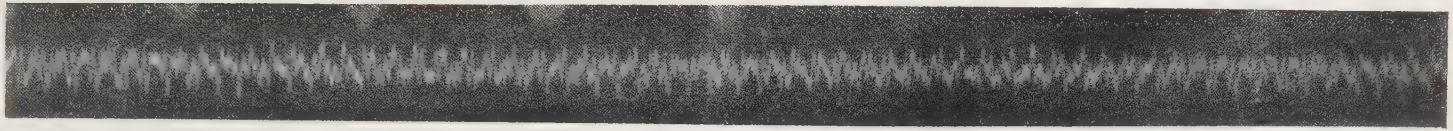
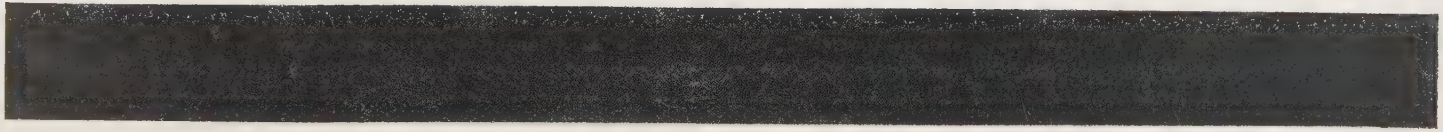



Fig. 4



# Sur la Propagation des Ondes de Dilatation dans la Mer

par

**Kiugoro Kitagawa**

(Reçu le 18 août, 1932)

**Sommaire**

Le présent travail a pour objet d'étudier la nature de la propagation des ondes de dilatation dans la mer. Nous commencerons par établir l'équation du mouvement de l'onde sonore

$$\frac{\partial^2\theta}{\partial t^2}=u^2{}_0(1+\alpha z)\Delta\theta+2u_0{}^2\alpha\frac{\partial\theta}{\partial z}$$

où $\theta$ désigne la dilatation cubique, $u_0$ la vitesse de la propagation d'une onde au niveau de la mer, $z$ la profondeur au point considéré.

Nous chercherons la solution générale de cette équation par la méthode des séries infinies et une solution approchée par la méthode des fonctions de Bessel.

Nous serons conduits de là à l'étude du trajet de la propagation d'une onde sonore, ce trajet étant une trajectoire orthogonale à une famille de courbes dépendant du paramètre temps et dont l'équation est représentée par la solution générale du mouvement. Le trajet du rayon sonore est dans le cas simple une courbe parabolique. Nous en calculerons la portée maxima, l'angle d'incidence, le rayon de courbure, et nous en déduirons la formule relative au sondage sonore.

## I. Préambule

Nous nous proposons d'étudier la propagation des ondes sonores dans la mer à une certaine profondeur. Nous envisagerons donc le cas d'ondes de dilatation sous-marines, se propageant à des distances, pouvant aller presqu'à 10 km. en été, 20 km. en hiver et parfois même 100 km[1]. On prétend qu'il est possible d'entendre avec des microphones des explosions sous-marines à des distances considérables, de l'ordre de 50 km. et plus, suivant l'importance de l'explosion. Les

1. MM. H. Barkhausen, H. Lichte, Ann. d. Phys. **62**, 485 (1920)

sons ordinaires peuvent de même se propager à des distances remarquables[1].

La densité des eaux marines dépend comme on sait de trois variables : pression, température et salinité[2].

Si l'on suppose la mer normale avec une salinité de 35 ‰ et à 0°C, la densité $\rho$ ne dépend que de la pression $p$ ; ces quantités sont d'une façon générale croissantes avec la profondeur. On peut donc admettre que $p$ et $\rho$ sont fonctions de la profondeur $z$ comptée en descendant à partir de la surface.

La profondeur $D$ s'exprime en mètres dynamiques, d'après M. Bjerknes[3], par la formule

$$D_2 - D_1 = \frac{1}{10}\int_{z_1}^{z_2} g_s dz$$

$g_s$ désignant l'accélération de la pesanteur au point considéré, prise le long du chemin $z_1 - z_2$.

En calculant cette intégrale, on obtient comme première approximation

$$D = 0.98z \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Grâce aux beaux tableaux[4] de M. Bjerknes, qui donnent la densité $\rho \times 10^5$ gr. et la pression $p$ décibars correspondant à une profondeur de $D$ mètres dynamiques, on peut trouver les accroissements $\delta p$ et $\delta\rho$ correspondant à un accroissement $\delta D = 100$ pour chaque point de

Tableau 1

| $D$ | 0 | 1000 | 2000 | 3000 | 4000 | 5000 |
|---|---|---|---|---|---|---|
| $\delta p$ | 102.837 | 103.33 | 103.80 | 104.27 | 104.73 | 105.18 |
| $\frac{\delta\rho}{\rho}\lambda$ | 49 | 48 | 47 | 46 | 45 | 45 |
| | 2.1 | 2.1 | 2.2 | 2.2 | 2.3 | 2.3 |
| $D$ | 6000 | 7000 | 8000 | 9000 | 9800 | |
| $\delta p$ | 105.62 | 106.06 | 106.48 | 106.91 | 107.24 | |
| $\frac{\delta\rho}{\rho}\lambda$ | 44 | 43 | 43 | 42 | 41 | |
| | 2.4 | 2.4 | 2.5 | 2.5 | 2.6 | |

1. M. E. Esclangon, l'Acoustique des Canons et des Projectiles, 205 (1925)
2. MM. V. Bjerknes and different collaborators, Dynamic Meteorology and Hydrography 1, 30 (1910)
3. M. Bjerknes, loc. cit. 14.
4. M. Bjerknes, loc. cit. Tableaux 15 H et 16 H.

profondeur $D$. On en déduit aisément pour le point envisagé la valeur approchée $\frac{\delta p}{\delta \rho}$, c'est à dire la valeur de l'expression $\frac{\lambda}{\rho}$, dans la mer normale, $\lambda$ étant le coefficient d'élasticité cubique (Tableau I).

La dernière ligne dans ce tableau, nous permet de poser onze équations observées de la forme

$$Dx+y=\frac{\lambda}{\rho}$$

où $D$ prend successivement les valeurs $D=0$, 1000, 2000.....9800, et $\frac{\lambda}{\rho}=2.1\times10^{10}$, $2.1\times10^{10}$.....$2.6\times10^{10}$.

En utilisant la méthode des moindres carrés, on obtient les équations normales suivantes :

$$381.04\times10^{6}x+54.8\times10^{3}y=132.98\times10^{13}$$

$$54.8\times10^{3}x+11y=25.6\times10^{10}$$

La résolutions de ce système nous donne :

$$5.04\times10^{5}D+2.08\times10^{10}=\frac{\lambda}{\rho}$$

Remplaçons $D$ par $z$ en vertu de (1), et prenons comme unité le centimètre au lieu du mètre, on obtient

$$V^2=v_0^2(1+\alpha z) \qquad \text{.....(2)}$$

avec

$$\left.\begin{aligned} V^2&=\frac{\lambda}{\rho},\quad v_0^2=\frac{\lambda_0}{\rho_0}=2.08\times10^{10}\\ \text{et}\\ \alpha&=2.38\times10^{-7}\end{aligned}\right\} \qquad \text{.....(3)}$$

Nous pouvons, d'autre part, établir pour un milieu liquide la relation

$$\frac{1}{\lambda}=-\frac{\theta}{p} \qquad \text{.....(4)}$$

en appelant $\theta$ la dilatation cubique, et $p$ la pression y correspondante.

Le coefficient d'élasticité cubique $\lambda$ est donné par une équation qui renferme les coefficients de déformation élastique ; nous pouvons considérer ces coefficients comme des fonctions des coordonnées du

point envisagé[1], et nous utiliser ainsi avec l'équation (2), la relation (4).

Dans l'eau, comme dans tous les liquides, il existe une certaine viscosité due au frottement interne, qui est fonction de pression et de température, et dont la valeur s'accroît lorsque la profondeur augmente ; mais nous négligerons cette correction et supposerons le liquide parfait.

## II. l'Équation fondamentale et son intégrale

Dans un milieu liquide, si $J_x$, $J_y$, $J_z$ désigne l'accélération d'une molécule en un point considéré $(x, y, z)$ à l'instant $t$, et si l'on suppose la force extérieure nulle, l'équation du mouvement est donnée par la formule :

$$\frac{\partial p}{\partial x}+\rho J_x=0, \text{ etc.}$$

Ces équations se transforment dans la mer, en tenant compte des relations (2), (3) et (4), et du fait que le déplacement est petit ; il vient

$$\left.\begin{aligned}\frac{\partial^2\xi}{\partial t^2}&=v_0^2(1+\alpha z)\frac{\partial\theta}{\partial x}\\ \frac{\partial^2\eta}{\partial t^2}&=v_0^2(1+\alpha z)\frac{\partial\theta}{\partial y}\\ \frac{\partial^2\zeta}{\partial t^2}&=v_0^2(1+\alpha z)\frac{\partial\theta}{\partial z}+v_0^2\alpha\theta\end{aligned}\right\} \quad \text{.....(5)}$$

en appelant $\xi$, $\eta$, $\zeta$ les composantes parallèles aux axes du déplacement élastique du point, et en prenant le niveau de la mer pour plan des $xy$, l'axe $z$ étant dirigé vers le bas. Pour l'équation de continuité, on aura

$$\frac{\partial}{\partial t}(\log\rho+\theta)=0$$

En dérivant respectivement les équations (5) par rapport à $x$, $y$, $z$ et en les ajoutant membre à membre, on obtient le résultat de la forme

$$\frac{\partial^2\theta}{\partial t^2}=v_0^2(1+\alpha z)\Delta\theta+2v_0^2\alpha\frac{\partial\theta}{\partial z} \quad \text{.....(6)}$$

C'est l'équation fondamentale de la propagation d'une onde de dilatation dans la mer.

1. M.A.E.H. Love, A Treatise on the Math. Theory of Elasticity, 107 (1927)

Nous allons maintenant aborder l'étude de l'intégrale de l'équation (6) ; on peut appliquer l'artifice habituel de produit. Posons

$$\theta = e^{i\sigma t} XZ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

en désignant par $X$ une fonction de la seule variable $x$, par $Z$ une fonction de la seule variable $z$, sans faire intervenir de fonction de $y$ en raison de la symétrie avec $x$.

En appliquant la relation (7) à l'équation (6), on obtient

$$\frac{1}{Z}\frac{d^2Z}{dz^2} + \frac{2a}{(1+az)Z}\frac{dZ}{dz} + \frac{\sigma^2}{v_0^2(1+az)} = -\frac{1}{X}\frac{d^2X}{dx^2}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

où les termes contenant les variables $x$ et $z$ sont comme on le voit séparés. On aura donc d'une part

$$\frac{d^2X}{dx^2} + n^2X = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

$n^2$ étant une constante. Son intégrale est de la forme

$$X = A_1 \sin nx + A_2 \cos nx \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

D'autre part,

$$(1+az)\frac{d^2Z}{dz^2} + 2a\frac{dZ}{dz} + \left\{\frac{\sigma^2}{v_0^2} - (1+az)n^2\right\}Z = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

C'est une équation différentielle de Laplace.

Posons ensuite

$$az = \xi \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

$\xi$ variant de zéro à 0.238, c'est-à-dire $z$ de zéro à $10^6$, l'équation obtenue par cette transformation est de la forme suivante

$$(1+\xi)\frac{d^2Z}{d\xi^2} + 2\frac{dZ}{d\xi} + (a-b-b\xi)Z = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

avec

$$a = \frac{\sigma^2}{v_0^2 a^2}, \quad b = \frac{n^2}{a^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

En opérant encore une fois la substitution suivante

$$Z = \frac{\xi^2}{1+\xi}\eta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (15)$$

il vient

$$\xi^2\frac{d^2\eta}{d\xi^2}+4\xi\frac{d\eta}{d\xi}+\left\{2+\frac{\xi^2}{1+\xi}(a-b-b\xi)\right\}\eta=0 \quad \ldots\ldots(16)$$

Cette équation admet, d'après le théorème de Fuchs, deux intégrales régulières distinctes dans le domaine contenant l'origine, parce que le coefficient de $\eta$ est fonction holomorphe dans ce domaine[1].

Remplaçons $\frac{1}{1+\xi}$ dans l'équation (16) par son développement en série ; on obtient

$$\xi^2\frac{d^2\eta}{d\xi^2}+4\xi\frac{d\eta}{d\xi}+\{2+(a-b)\xi^2-a\xi^3+a\xi^4\ldots+(-1)^m a\xi^m+\ldots\}\eta=0$$
$$\ldots\ldots(17)$$

Remplaçons $\eta$ dans le premier membre de l'équation (17) par un développement de la forme

$$\eta=c_0\xi^r+c_1\xi^{r+1}+c_2\xi^{r+2}+\ldots\ldots+c_m\xi^{r+m}+\ldots\ldots,(c_0\neq 0)$$
$$\ldots\ldots(18)$$

$c_0$, $c_1\ldots\ldots c_m\ldots\ldots$ étant des coefficients que nous prendrons de la façon suivante : Égalons à zéro le terme en $\xi^r$, il viendra

$$\left.\begin{aligned} &c_0\{r(r-1)+4r+2\}=0\\ \text{d'où}\quad &r=-1 \quad \text{ou} \quad -2\end{aligned}\right\} \ldots\ldots(19)$$

Prenons pour $r$ l'une des deux valeurs trouvées, et choisissons $c_0$ arbitrairement. En posant par exemple $r=-1$, $c_0=1$ et en égalant encore à zéro le terme en $\xi^{r+p}$, on aura

$$c_p\{(r+p)(r+p-1)+4(r+p)+2\}+(a-b)c_{p-2}-ac_{p-3}+ac_{p-4}+\ldots=0$$

Cette formule permet de calculer de proche en proche les coefficients successifs $c_1$, $c_2\ldots\ldots c_m$, en faisant successivement $p=1,2\ldots\ldots m$, car l'équation n'admet pas de seconde racine qui soit égale à la première $-1$ augmentée d'un nombre entier positif. Nous aurrons donc une intégrale particulière donnée par la formule (18), à savoir

$$\eta_1=\xi^{-1}\varphi(\xi) \quad \ldots\ldots(20)$$

où

$$\varphi(\xi)=1-\frac{a-b}{6}\xi^2+\frac{a}{12}\xi^3+\ldots\ldots, \quad \ldots\ldots(20\text{ bis})$$

$\varphi(\xi)$ étant une fonction holomorphe qui ne s'annule pas pour $\xi=0$, et

1. M. E. Goursat, Cours d'Analyse mathématique, **2**, 476 (1929)

dont la convergence a été demontrée par M. Goursat dans son cours cité plus haut. La différence des deux racines de l'équation (19) étant un nombre entier, on obtient une seconde intégrale particulière $\eta_2$ par la formule générale suivante :

$$\eta_2=\eta_1\int_{\xi_0}^{\xi}\frac{d\xi}{\eta_1^2}e^{-\int_{\xi_0}^{\xi}\frac{4}{\xi}d\xi}=\xi^{-2}\psi(\xi) \quad \ldots\ldots\ldots\ldots\ldots\ldots(21)$$

où

$$\psi(\xi)=-1+\frac{a-b}{2}\xi^2-\frac{a}{6}\xi^3+\ldots\ldots, \quad \ldots\ldots\ldots\ldots\ldots\ldots(21\text{ bis})$$

La solution générale est donc de la forme

$$\eta=B_1\xi^{-1}\varphi(\xi)+B_2\xi^{-2}\psi(\xi) \quad \ldots\ldots\ldots\ldots\ldots\ldots(22)$$

d'où l'on tira la solution générale de l'équation (13)

$$Z=B_1\Phi(\xi)+B_2\Psi(\xi) \quad \ldots\ldots\ldots\ldots\ldots\ldots(23)$$

avec

$$\left.\begin{aligned}\Phi(\xi)&=\xi-\xi^2+\left(1-\frac{a-b}{6}\right)\xi^3+\left(\frac{3a-2b}{12}-1\right)\xi^4+\ldots\\ \Psi(\xi)&=-1+\xi+\left(\frac{a-b}{2}-1\right)\xi^2+\left(1-\frac{4a-b}{6}\right)\xi^3+\ldots\end{aligned}\right\}(23\text{ bis})$$

Nous pouvons ainsi donner à l'équation (7) l'aspect suivant

$$\theta=e^{i\sigma t}\{A_1\sin nx+A_2\cos nx\}\{B_1\Phi(\alpha z)+B_2\Psi(\alpha z)\}\ldots(24)$$

formule qui représente la solution générale de l'équation fondamentale.

## III. Une solution approchée par la méthode des équations de Bessel

Opérons dans l'équation (13) la substitution suivante

$$Z=\frac{\eta}{1+\xi} \quad \ldots\ldots\ldots\ldots\ldots\ldots(25)$$

il vient

$$\frac{d^2\eta}{d\xi^2}+\left(\frac{a}{1+\xi}-b\right)\eta=0 \quad \ldots\ldots\ldots\ldots\ldots\ldots(25\text{ bis})$$

C'est une équation différentielle linéaire spéciale du second ordre, $\xi$

variant de zéro à 0.238. M. Picard[1] donne dans son cours une étude approfondie d'équations semblables à l'équation (25 bis), en opérant des approximations successives, et en utilisant avec M. Schwarz deux séries de constantes.

En remplaçant la fonction $\frac{a}{1+\xi}$ par son développement en série et en négligeant les puissances supérieures à $\xi^2$, l'équation (25 bis) devient

$$\frac{d^2\eta}{d\xi^2}+(a-b-a\xi)\eta=0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(26)$$

Opérons la transformation suivante :

$$\eta=(a-b-a\xi)^{\frac{1}{2}}v,\ a-b-a\xi=\left(\frac{3}{2}a\zeta\right)^{\frac{2}{3}} \quad \ldots\ldots\ldots\ldots(26\text{ bis})$$

L'équation (26) prend la forme

$$\zeta^2\frac{d^2v}{d\zeta^2}+\zeta\frac{dv}{d\zeta}+\left(\zeta^2-\frac{1}{9}\right)v=0 \quad \ldots\ldots\ldots\ldots\ldots\ldots(27)$$

Nous avons là une équation de Bessel. En posant successivement $n=\frac{1}{3}$ et $n=-\frac{1}{3}$, nous obtenons deux intégrales de cette équation sous la forme des séries :

$$J_n(\zeta)=\sum_{r=0}^{\infty}\frac{(-1)^r\left(\frac{\zeta}{2}\right)^{n+2r}}{\lfloor r\,\Gamma(n+r+1)}$$

Ces intégrales $J_{\frac{1}{3}}$, $J_{-\frac{1}{3}}$ sont évidemment indépendantes, car l'ordre n'est pas un entier réel ; l'intégrale générale est donc de la forme

$$v=C_1J_{-\frac{1}{3}}(\zeta)+C_2J_{\frac{1}{3}}(\zeta) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(27\text{ bis})$$

## IV. Trajet de propagation de l'onde sonore

Nous venons de trouver la solution de l'équation fondamentale (6). Soit l'intégrale (7)

$$\theta=e^{i\sigma t}XZ,$$

l'équation d'une famille de courbes $\Gamma$, dépendant d'un paramètre arbitraire $t$. Si l'on cherche la courbe $L$

$$z=f(x) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(28)$$

1. M. E. Picard, Traité d'Analyse, **3**, 100 (1928)

qui coupe orthogonalement en chacun de ses points la courbe $\Gamma$ passant par ce point, la courbe $L$ est la trajectoire orthogonale. La condition d'orthogonalité entre (7) et (28) se réduit à l'équation linéaire

$$\frac{\partial\theta}{\partial x}\frac{dz}{dx}-\frac{\partial\theta}{\partial z}=0$$

Les courbes caractéristiques, dont l'équation différentielle est de la forme

$$\frac{dx}{\frac{\partial\theta}{\partial x}}=\frac{dz}{\frac{\partial\theta}{\partial z}}$$

c'est-à-dire

$$\int\frac{dx}{\frac{1}{X}\frac{dX}{dx}}=\int\frac{dz}{\frac{1}{Z}\frac{dZ}{dz}} \qquad \text{.....(29)}$$

sont des courbes qui, en chacun de leur points, admettent pour tangente la normale à la courbe $\Gamma$ passant par ce point, c'est-à-dire des courbes qui représentent le trajet de la propagation de l'onde sonore.

Intégrons l'équation (29), en prenant le cas simple où, en vertu des relations (10), (12), (25) et (26 bis),

$$X=\sin nx,\quad Z=\frac{(a-b-a\alpha z)^{\frac{1}{2}}}{1+\alpha z}J_{-\frac{1}{3}}(\zeta)$$

On aura le résultat suivant :
d'une part

$$\int-\frac{\frac{dx}{\frac{1}{\sin nx}\cdot\frac{d\sin nx}{dx}}}{}=-\frac{1}{n^2}\log\cos nx \qquad \text{.....(30)}$$

d'autre part

$$\log Z=\frac{1}{2}\log(a-b-a\alpha z)-\log(1+\alpha z)+\log J_{-\frac{1}{3}}(\zeta)$$

On obtient donc, en tenant compte des relations

$$\zeta=\frac{2}{3a}(a-b-a\alpha z)^{\frac{3}{2}},\quad\frac{d\zeta}{dz}=-\alpha(a-b-a\alpha z)^{\frac{1}{2}}$$

et

$$\frac{dJ_{-\frac{1}{3}}(\zeta)}{d\zeta}=-\frac{J_{-\frac{1}{3}}(\zeta)}{3\zeta}-J_{\frac{2}{3}}(\zeta),^{1}$$

$$\frac{1}{Z}\frac{dZ}{dz}=\frac{1}{2}\frac{-a\alpha}{a-b-a\alpha z}-\frac{a}{1+\alpha z}+\frac{1}{J_{-\frac{1}{3}}(\zeta)}\cdot\frac{dJ_{-\frac{1}{3}}(\zeta)}{d\zeta}\cdot\frac{d\zeta}{dz}$$

$$=-\frac{a}{1+\alpha z}+a(a-b-a\alpha z)^{\frac{1}{2}}\frac{J_{\frac{2}{3}}(\zeta)}{J_{-\frac{1}{3}}(\zeta)} \quad \text{.....(31)}$$

En négligeant les puissances plus élevées de $x$, $z$, $\zeta$ et en supposant $a-b=0$, on peut trouver une valeur approchée des expressions (30) et (31), bien suffisante pour les besoins pratiques[2]. On aura comme première approximation

$$\frac{J_{\frac{2}{3}}(\zeta)}{J_{-\frac{1}{3}}(\zeta)}\fallingdotseq\frac{3}{4}\zeta$$

La formule (31) devient alors

$$\frac{1}{Z}\frac{dZ}{dz}\fallingdotseq-\frac{a}{1+\alpha z}+\frac{a\alpha^{3}z^{2}}{2}\fallingdotseq-\frac{a}{1+\alpha z}$$

On a de même

$$\int\frac{dz}{\frac{1}{Z}\frac{dZ}{dz}}=-\int\frac{1+\alpha z}{a}dz\fallingdotseq-\frac{z}{a} \quad \text{.....(32)}$$

En égalant (30) et (32), il vient

$$\log\cos nx=\frac{n^{2}}{a}z+C$$

c'est-à-dire

$$\cos nx=e^{\frac{n^{2}z}{a}} \quad \text{.....(33)}$$

en faisant correspondre $x=o$ à $z=o$.

Développons en séries les deux membres de (33), et négligeons les puissances plus élevées de $x$ et de $z$ ; nous obtenons

$$1-\frac{n^{2}x^{2}}{2}\fallingdotseq1+\frac{n^{2}}{a}z$$

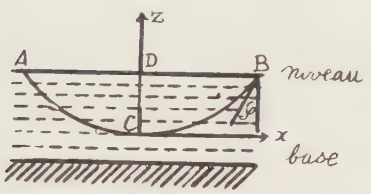
1. MM. R. Courant und D. Hilbert, Methoden der math. Physik, **1**, 421 (1931)
2. Lord Rayleigh, The Theory of Sound, **2**, 131 (1926)

En changeant le sens des $z$ comptés maintenant vers le haut, nous arrivons à l'équation à forme parabolique suivante :

$$x^2 = \frac{2}{a} z \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (34)$$

Cette formule représente dans le cas simple l'équation du trajet de la propagation d'une onde sonore dans la mer.

Fig 1




La profondeur $CD = z$ étant donnée, on peut calculer la portée $AB$ (fig. 1).

$$AB = 2x = 2\sqrt{\frac{2z}{a}} \qquad \ldots\ldots\ldots (35)$$

L' angle d'incidence $\varphi$ est donné par la formule

$$\tan\varphi = \frac{dx}{dz} = \frac{1}{\sqrt{2az}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (36)$$

et le rayon de courbure $R$,

$$R = \frac{(1 + z'^2)^{\frac{3}{2}}}{z''} = \frac{1}{a}(1 + 2az)^{\frac{3}{2}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (37)$$

Nous pouvons établir les valeurs numériques suivantes :

| CD = $z$ | AB = $2x$ | $\varphi$ | R à A et à B |
|---|---|---|---|
| $4 \times 10^5$ cm. | $3.67 \times 10^8$ | 66°25'30" | $5.46 \times 10^8$ |
| $10^8$ cm. | $5.80 \times 10^8$ | 55°23'50" | $7.53 \times 10^8$ |

## V. Durée de propagation d'une onde sonore

Pour connaître la durée que met le rayon sonore à aller d'un point à un autre, il faut calculer l'intégrale entre deux points du milieu du trajet

$$t = \int \frac{ds}{V} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (38)$$

en désignant par $ds$ l'élément de trajet, et par $V$ la vitesse variable (2).

L'équation (34) nous donne d'une part

$$ds = \sqrt{1 + a^2x^2}\, dx$$

l'équation (2), d'autre part

$$V=u_0\sqrt{1+\alpha(z_1-z)}=u_0\sqrt{1+\frac{\alpha^2}{2}(x_1^2-x^2)}$$

$x_1$, $z_1$ étant les coordonnées du niveau. On aura donc

$$t=\int_0^x \frac{\sqrt{1+\alpha^2x^2}\,dx}{u_0\sqrt{1+\frac{\alpha^2}{2}(x_1^2-x^2)}}=\frac{\sqrt{2}}{\alpha u_0}\int_o^q \sqrt{\frac{1+q^2}{2+q_1^2-q^2}}\,dq$$

.....(39)

en posant $\alpha x=q$, $\alpha x_1=q_1$. Cette formule se réduit à

$$t=\frac{\sqrt{2}}{\alpha u_0}\sqrt{3+q_1^2}\int_\omega^1 \frac{1-k^2\omega^2}{\sqrt{(1-k^2\omega^2)(1-\omega^2)}}d\omega \quad .....(40)$$

avec

$$\omega=\sqrt{1-\frac{q^2}{2+q_1^2}}<1,\quad k^2=\frac{2+q_1^2}{3+q_1^2}<1$$

Nous sommes donc ramenés à une intégrale elliptique, et avec les notations de Tannery[1], on aura dans ce cas,

$$a_0=k^2,\ 4a_1=0,\ 6a_2=-(1+k^2),\ 4a_3=0,\ a_4=1$$

$$\int\frac{d\omega}{\sqrt{(1-k^2\omega^2)(1-\omega^2)}}=C_1+u$$

et

$$k^2\int\frac{\omega^2d\omega}{\sqrt{(1-k^2\omega^2)(1-\omega^2)}}=C_2+\frac{1+k^2}{6}u-\zeta(u+v)-\zeta u$$

On a donc

$$\int\frac{1-k^2\omega^2}{\sqrt{(1-k^2\omega^2)(1-\omega^2)}}d\omega=C+\frac{5-k^2}{6}u+\zeta(u+v)+\zeta u$$

L'équation (40) devient alors

$$t=\frac{\sqrt{2(3+q_1^2)}}{\alpha u_0}\left[C+\frac{5-k^2}{9}u+\zeta(u+v)+\zeta u\right] \quad .....(41)$$

Pour calculer les valeurs approchées, développons la fonction (39) en série de Taylor ; on aura

1. J. Tannery et J. Molk, Éléments de la Théorie des Fonctions elliptiques, **4**, 156 (1902)

$$f(q)=\sqrt{\frac{1+q^2}{2+q_1^2-q^2}}=\frac{1}{\sqrt{2+q_1^2}}+\frac{q^2}{\underline{|2}}\times\frac{3+q_1^2}{(2+q_1^2)^{\frac{3}{2}}}+\ldots\ldots$$

et par conséquent

$$t=\frac{\sqrt{2}}{au_0}\int_0^q f(q)dq=\frac{\sqrt{2}}{au_0}\left\{\frac{q}{\sqrt{2+q_1^2}}+\frac{q^3}{\underline{|3}}\times\frac{3+q_1^2}{(2+q_1^2)^{\frac{3}{2}}}+\ldots\ldots\right\}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(42)$$

On en déduit comme première approximation

$$t=\frac{\sqrt{2}}{au_0}\frac{q}{\sqrt{2+q_1^2}}=\frac{\sqrt{2}}{au_0}\sqrt{\frac{az}{1+az_1}}\quad\ldots\ldots\ldots\ldots\ldots\ldots(43)$$

On obtient donc, pour la durée $T_1$ que met le rayon sonore à aller le long de la courbe $ACB$ (fig. 1),

$$T_1=2t=\frac{2x_1}{u_0}\frac{1}{\sqrt{1+az_1}}$$

Comme la durée $T_2$ que le son met à aller le long de la droite $AB$ est donné par la formule :

$$T_2=\frac{2x_1}{u_0}$$

On en conclut

$$T_1=T_2\times\frac{1}{\sqrt{1+az_1}}\quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(44)$$

Par exemple, pour $z_1=4\times10^5$ cm., on a $\frac{1}{\sqrt{1+az_1}}\doteq0.95$ et $T_1$ est plus court que $T_2$ de 5%.

## VI. Formule relative au sondage sonore

Nous nous limiterons au seul cas à envisager dans la pratique du sondage acoustique, celui où le rayon sonore tombe presque verticalement. La durée $T$ que le rayon met à aller du niveau $z=0$ à la profondeur $z$ et revenir est donné évidemment par la formule :

$$T=2\int_0^z\frac{dz}{u_0\sqrt{1+az}}=\frac{4}{au_0}(\sqrt{1+az}-1)$$

d'où l'on tire

$$z=\frac{u_0T}{2}+\frac{au_0^2T^2}{16}-\quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(45)$$

Nous avons là l'équation relative au sondage sonore dans le cas où la vitesse varie avec la profondeur. Dans le cas où la vitesse du son est constante, on peut négliger le dernier terme et on obtient

$$z = \frac{u_0 T}{2}$$

Indiquons les valeurs de $z$ dans les trois cas suivants :

| $T_{sec}$ | $\frac{u_0 T}{2}$ | $\frac{\alpha u^2_0 T^2}{16}$ | $z$ cm. |
|---|---|---|---|
| 2 | $1.44 \times 10^5$ | $0.01 \times 10^5$ | $1.45 \times 10^5$ |
| 5 | 3.60 „ | 0.08 „ | 3.68 „ |
| 10 | 7.21 „ | 0.31 „ | 7.52 „ |

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# On the Chemistry of Japanese Plants X. Utilisation of Plant Ash in Chemical Industries I.

By

**Shigeru Komatsu** and **Yoshiharu Ogata**

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"Koji" which is made from "Tane-koji" or Moyashi, leaven and steamed rice, is mixed with steamed rice in order to make Sake, the common beverage of Japan. In the process the rice starch is converted into alcohol by the enzymatic action of Aspergillus oryzae grown in the Koji.[1]

Tane-koji, a yellowish green powder consisting of the spores of Aspergillus oryzae, is prepared both in Sake breweries and in special works, as it is used for various purposes in Japan besides Sake making.

In the preparation of Tane-koji,[2] the polished rice is boiled by steam; to it are added 1 m. of rice and 0.2 m. of a plant ash, and the whole is packed in straw matting and placed on stands in the kiln. After the lapse of ten days, mould developes.

The writers have interested themselves in the process of the preparation of Tane-koji and especially in the use of plant ash. The Koji works in Kyoto use for making Koji plant ash prepared by burning in air the young twigs of the Hoso-tree, Quercus senata Thumberg, grown at Ohara, near Kyoto City, gathered in summer and dried in the shade, but the ash from soy bean stems is usually employed for making an inferior kind of Koji. We also learn from "The History of Sake-making at Nada[3]" that Tane-koji is prepared there from steamed rice and plant ash obtained from the young leaves of the Nara or Tsubaki which are gathered in summer and dried in the shade.

1. K. Yabe & S. Sugiyama: The Brewing Industry of Japan; Industrial Japan 530–547 (1929); R. W. Atkinson: Studies on Sake. (1880–1881).
2. J. J. Hoffman: Sake Brewing in Japan (1872).
3. In Japanese, in referring the writers' thanks to Mr. Y. Tatsuma.

According to R. W. Atkinson[1] who has made a comparative study of polished rice and Koji by analysis, the formation of Koji is an illustration of the growth of the mycelium of a fungus which uses the starch of the rice grain as food.

Table I

| | Whitened rice dried at 100° | Koji dried at 100° |
|---|---|---|
| Starch | 82.27 % | 56.00 % |
| Cellulose | 4.79 „ | 4.20 „ |
| Dextrose & dextrin | 1.91 „ | 28.90 „ |
| Fat | 0.49 „ | 0.43 „ |
| Albumenoides | 9.45 „ | 9.84 „ |
| Ash | 1.09 „ | 0.61 „ |

However, the writers' opinion is that some of the ash constitutents in Koji have an intimate connection with the growth of the organism; in other words, they play an important rôle in the conversion of the starch molecule of the rice into $CO_2$ and water and other organic compounds of lower molecular weight, and the energy released by the process is used for the growth of organism.

Referring to the literature,[2] we noticed that the ash prepared from Sake-yeast and spores of Koji was mostly composed, as may be seen in Table I, of P, K & Mg.

The results[3] of analysis of the ash from yeasts of various sources also show that the elements K, P, Ca and Mg are its chief constituents.

Table II

| | Ash of yeast | Ash | |
|---|---|---|---|
| | | Sake-yeast | Spores of Koji |
| $K_2O$ | 23.33 — 39.5 % | 31.9 | 45.9 |
| $Na_2O$ | 0.5 — 2.26 „ | 17.6 | 4.1 |
| CaO | 1.0 — 7.58 „ | trace | 1.1 |
| MgO | 3.77 — 6.34 „ | 5.9 | 4.4 |
| $Fe_2O_3$ | 0.06 — 0.7 „ | — | 4.9 |
| $P_2O_5$ | 44.8 — 59.4 „ | 44.5 | 39.6 |
| $SO_3$ | 0.57 — 6.35 „ | 0.4 | 2.0 |
| $SiO_2$ | 0.92 — 1.88 „ | — | 0.4 |

1. Loc. cit.
2. K. Kurono: Handbook of Physiology of Fermentation (Japanese) (1927) p. 420.
3. E. Duclaux: Traité de microbiologie III, 135 (1900); H. Euler & P. Lindner: Chemie der Hefe (1915) p. 72.

From these reports, it may be supposed that such inorganic elements as K, P, Ca & Mg, which constitute the greater part of the ash of yeast and Koji have an intimate connection with the development of Aspergillus oryzea which uses the starch of the rice as food, and accordingly these inorganic materials are supplied to accomplish the metabolism of the starch in the living cells from the plant ash employed in the preparation of Tane-koji. This idea is partly illustrated by reference to the analysis of the ash from soy bean stems and the Nara-tree.

Table III

| | $K_2O$ | $Na_2O$ | CaO | MgO | $P_2O_5$ | $SO_3$ | $SiO_2$ |
|---|---|---|---|---|---|---|---|
| Soy bean stems | 15.3 | 2.1 | 44.6 | 15.3 | 10.0 | 6.4 | 5.5 |
| Nara-tree | 44.6 | 2.2 | 40.0 | 7.9 | 4.3 | 0.2 | 3.3 |

The ash of the Hoso-tree is, therefore, used simply as a source of potassium, calcium, magnesium and phosphorus, which are important inorganic materials in the metabolism of starch in the Aspergillus oryzae, and it may be assumed that the reason why the plants are gathered in summer is that there is an abundance of these elements in the plant tissues in this season. The present study of the seasonal variation of ash constituents, was therefore undertaken by the writers to confirm this supposition.

The samples used for the experiment, twigs one or two years old, were gathered once a month from 10 to 11 o'clock on fine mornings from 18 trees growing on a mountain slope about 120 $m^2$ in area in the Gosho-tani forest, Hanazono, Iwakura, Kyoto, located about 4 miles from the laboratory.

Each sample was divided into two parts, leaves and twigs, and weighed and dried to constant weight in an air bath at 105°, and the loss of weight was designated moisture-content.

The samples, dried as above, were incinerated in the usual way; the crude ash, prepared by burning in a platinum crucible with an alcohol lamp, was treated with water to extract the soluble constituents, and the insoluble residue was again heated in an electric oven at 600°.

The results given in the table show the mean value obtained in three experiments.

Table IV

| | | Wt. of dried sample | T/L (ratio of twig (T) to leaf (L)) |
|---|---|---|---|
| 17/IV | (T) | 176 gms. | — |
| | (L) | — | — |
| 15/V | (T) | 144 | 0.9 |
| | (L) | 166 | |
| 15/VI | (T) | 142 | 1.0 |
| | (L) | 142 | |
| 16/VII | (T) | 166 | 1.0 |
| | (L) | 159 | |
| 31/VII | (T) | 250 | 1.5 |
| | (L) | 162 | |
| 15/VIII | (T) | 140 | 1.2 |
| | (L) | 118 | |
| 16/IX | (T) | 182 | 1.4 |
| | (L) | 130 | |
| 15/X | (T) | 210 | 1.7 |
| | (L) | 123 | |
| 15/XI | (T) | 180 | 0.9 |
| | (L) | 195 | |
| 19/XII | (T) | 139 | — |
| 27/I | (T) | 140 | — |

The ratio of dry weight of twigs to that of leaves, as may be seen in the table, increased gradually from 0.9 to 1.7 and then decreased to 0.9, depending mostly upon their water-content.

The percentage of water and ash in twigs and leaves changes with the months in the following manner:—

Table V

| | Twig | | Leaf | | Twig+Leaf |
|---|---|---|---|---|---|
| | $H_2O$ % | Ash % | $H_2O$ % | Ash % | Ash % |
| IV | 43.51 | 2.93 | 64.60 | 4.10 | — |
| V | 68.17 | 4.72 | 68.71 | 4.49 | 4.37 |
| VI | 53.86 | 4.12 | 57.0 | 5.18 | 4.65 |
| VII (16) | 48.14 | 3.04 | 54.07 | 5.24 | 4.14 |
| VII (31) | 51.67 | 2.99 | 59.37 | 5.26 | 4.87 |
| VIII | 52.11 | 3.12 | 58.85 | 5.31 | 4.53 |
| IX | 48.05 | 2.39 | 56.10 | 5.24 | 4.29 |
| X | 48.16 | 3.31 | 54.54 | 4.94 | 3.88 |
| XI | 52.87 | 3.49 | 45.00 | 4.14 | 3.63 |
| XII | 46.07 | 4.05 | fallen | — | 4.03 |
| I | 50.79 | 4.15 | fallen | — | 4.15 |

The monthly change in the ash content of the twigs runs parallel with that of the water content, showing a maximum in May and a minimum in September, but in the case of the leaf, the monthly change in these constituents is different, the water content diminishing gradually with time from 65 % to 45 % though the ash content shows a maximum in August. However, the average ash content of twigs and leaves shows a maximum in summer.

The chemical composition of the ash both of twigs and leaves was studied by analysis with the following results (Table VI).

As may be seen in Table VI, the content of elements in both twigs and leaves changes with the month, and $P_2O_5$ and $K_2O$ in the twigs show the highest percentage in August and July respectively (15 % and 30 %), but in leaf-ash these compounds show a high percentage at the end of spring and then their content decreases gradually with time. The content of both Mg and Mn, however, is the maximum in summer.

From the seasonal variation of the content of the ash constituents expressed on the dry bases of twigs and leaves, shown in Table VII, we learned that such elements as P, K and Mg are accumulated abundantly in the plant tissues in summer.

As a matter of fact, the essential elements of the ash of Sake-yeast and Koji-spores are found as the chief constituents of the ash of Hoso-trees in the stage of vigorous growth and also of soy bean stems and the Nara-tree, and thus the biochemical significance of the use of plant ash in Koji-making is explained ; it supplies the inorganic elements which facilitate the development of the organism.

"Moyashi," as mentioned above, is prepared in Japan by the method handed down from ancient times, a method unknown to western peoples. The essential part of this method is here explained biochemically ; it being supposed that the inorganic elements which occur in the active parts of plant tissues play an essential part when they enter the body of a micro organism, in the process of the metabolism of organic material, this view was confirmed by the study of the seasonal variation of the ash constituents.

It is the desire of one of the writers (S. K.) to devote himself to the biochemical study of oriental customs or phases of oriental civilization which are based on the utilization of indigenous natural substances as a means of supporting or enriching life.

Table VI

| | $SiO_2$ | $SO_3$ | $P_2O_5$ | $Al_2O_3$ | $Fe_2O_3$ | $Mn_3O_4$ | CaO | MgO | $K_2O$ | $Na_2O$ | Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|
| IV | 42 | 15 | 33 | — | 10 | 8 | 85 | 17 | 64 | 10 | 1 |
| V | 36 (twigs) | 28 | 54 | 4 | 12 | 10 | 151 | 13 | 125 | 21 | 4 |
| | 93 (leaves) | 25 | 36 | 1 | 9 | 4 | 117 | 26 | 123 | 10 | 4 |
| VI | 12 | 13 | 49 | 7 | 10 | 14 | 161 | 17 | 95 | 8 | 3 |
| | 122 | 26 | 37 | 1 | 7 | 5 | 146 | 34 | 128 | 10 | |
| VII | 13 | 11 | 43 | 5 | 6 | 10 | 80 | 17 | 92 | 11 | 3 |
| | 148 | 26 | 33 | 8 | 4 | 12 | 118 | 33 | 113 | 11 | 4 |
| | 11 | 10 | 42 | 5 | 4 | 9 | 102 | 15 | 84 | 9 | 2 |
| | 150 | 22 | 33 | 7 | 10 | 13 | 109 | 32 | 111 | 5 | 4 |
| VIII | 10 | 9 | 47 | 2 | 5 | 9 | 104 | 14 | 91 | 9 | 3 |
| | 156 | 22 | 34 | 5 | 9 | 12 | 110 | 31 | 114 | 7 | 3 |
| IX | 7 | 7 | 31 | 6 | 2 | 9 | 86 | 15 | 60 | 6 | 1 |
| | 161 | 24 | 31 | 5 | 6 | 18 | 119 | 30 | 107 | 14 | 4 |
| X | 26 | 17 | 27 | 2 | 5 | 19 | 113 | 17 | 71 | 12 | 2 |
| | 192 | 22 | 27 | 2 | 4 | 5 | 125 | 17 | 62 | 15 | 1 |
| XI | 17 | 11 | 31 | 3 | 2 | 12 | 133 | 19 | 76 | 19 | 2 |
| | 151 | 9 | 20 | 3 | 6 | 11 | 118 | 18 | 54 | 8 | 1 |
| XII | 16 | 18 | 15 | 4 | 4 | 11 | 179 | 19 | 87 | 27 | 5 |
| I | 11 | 14 | 31 | 5 | 4 | 11 | 174 | 26 | 90 | 27 | 5 |

The ash content of leaves, as may be seen in Table V, drops suddenly before the autumn leaf-fall, while that of twigs increases after that season, and this fact is explained by assuming that some of the inorganic elements migrate from the former to the latter before autumn comes. The assumption that the loss of ash in leaves is balanced by an accumulation in the twigs may be confirmed by the fact that the average ash content, both of twigs and leaves, as is seen in Table V, remains almost constant after spring has passed. However, the percentage of ash constituents expressed on water free bases shows that when autumn comes the content of P, Al, Mn, Ca, Na and Si is decreased in both leaf and twig. This is probably due to the fact that they are given off from the plant by the fallen-leaf in the form of mineral matter and of organic constituents, a view put

forward in the "Biochemical Study on the Autumn Fall of the Leaf" by one of the writers (S. K.) and Ozawa[1]. There it is stated that one of the most important functions of the autumn leaf-fall is to enable the plant to get rid of inorganic materials—ash—so that the accumulated ash constituents are prevented from controlling the metabolic changes of the tissue materials and the plant is able to live a normal life in winter.

The inorganic elements in the Hoso-tree are divided biochemically into three classes: (1) elements like Si, the content of which increases with time: (2) those like S, P & K which decrease as the season progresses, and (3) such elements as Al, Mn, Mg and Ca which show a maximum or minimum in their seasonal change. The characteristics of the elements in their seasonal variation are probably intimately connected with the functions of these elements in the vital processes of plant tissues. The functions of the elements in the life of the plant are supposed to be different from each other; the elements which belong to the first class probably give rigidity and comparative permanense to the plant skeleton, and those belonging to the second and the third class are regarded as taking part in metabolism or photosynthesis.

It is to be supposed that the inorganic elements which function in the metabolic process of the organic matter in plants—the germination of seeds and budding etc.—will be found abundantly in the ash obtained from plants in the stages of vigorous growth. Such elements as Ca, Mg, P & K which constitute the major part of the ash of leaves of the Hoso-tree gathered in summer will partly migrate from leaf to twig before the autumn leaf-fall in order to prepare for the budding or vital processes in the plant tissues in the following spring.

April 1928, Laboratory of Organic & Bio-Chemistry.

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1. These Memoirs, **15**, 57 (1932).

Fig. 1

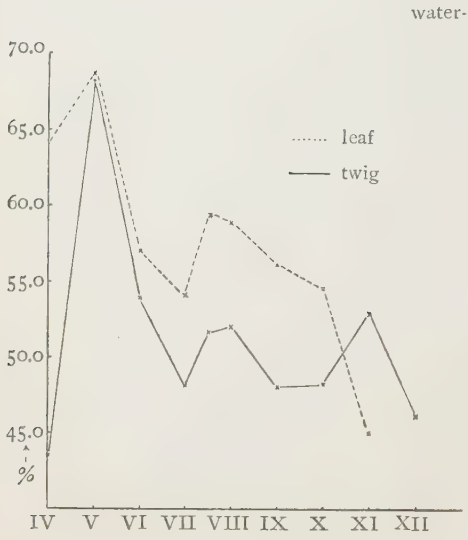



Fig. 3

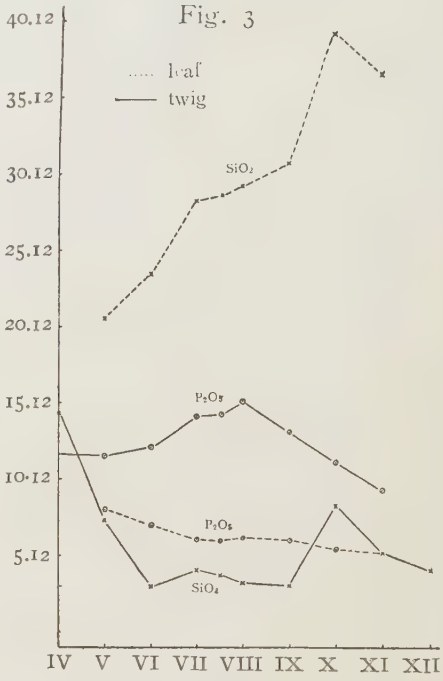



Fig. 2

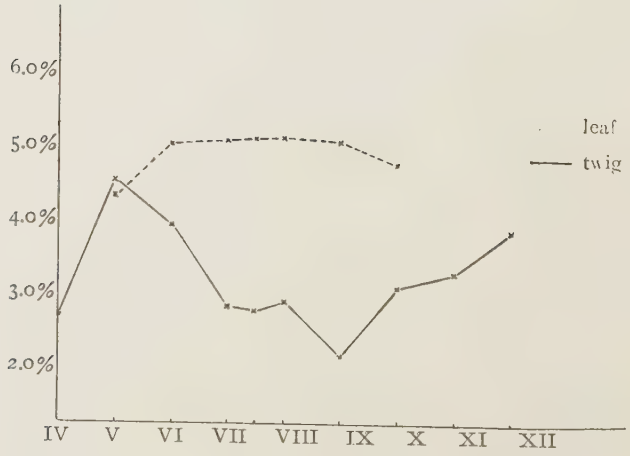


Fig. 4

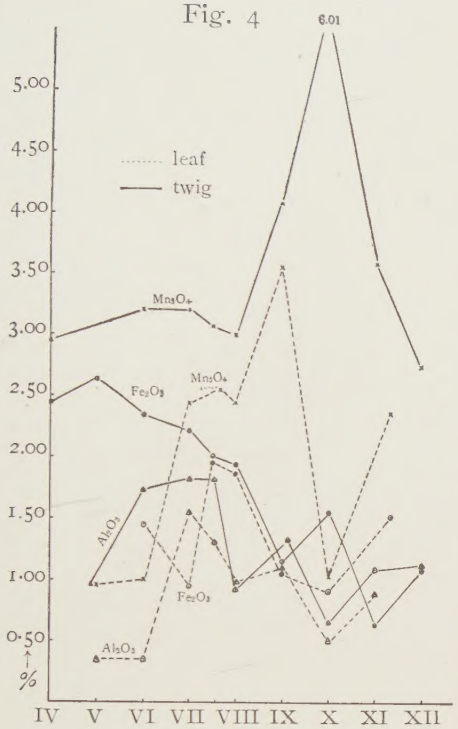



Fig. 5

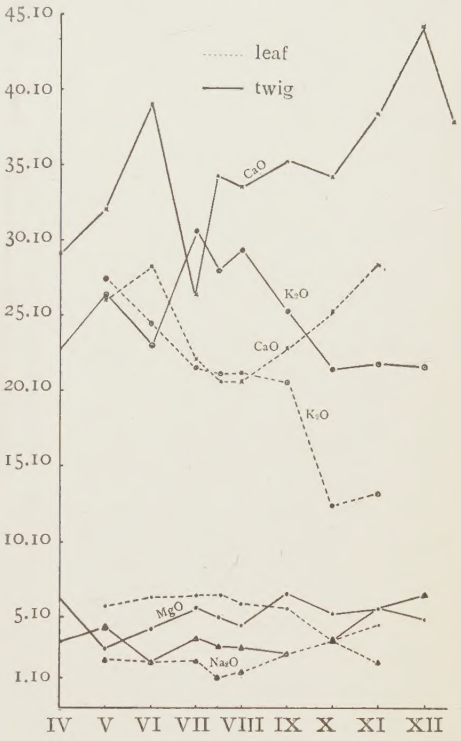
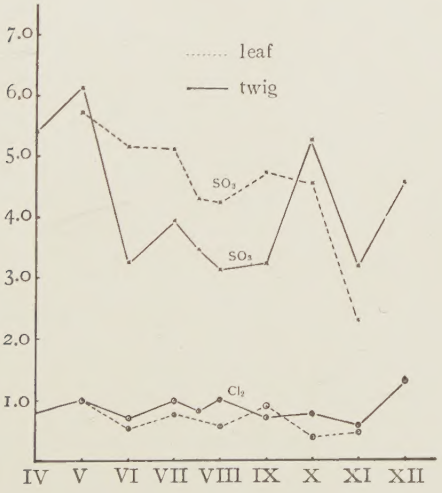



Fig. 6



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